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# E WATERPROOFING OF FABRICS

Dr. S. MIERZINSKI

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# THE WATERPROOFING OF FABRICS

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OF

# FABRICS

BY

DR. S. MIERZINSKI

TRANSLATED FROM THE GERMAN

BY

ARTHUR MORRIS AND HERBERT ROBSON, B.Sc.

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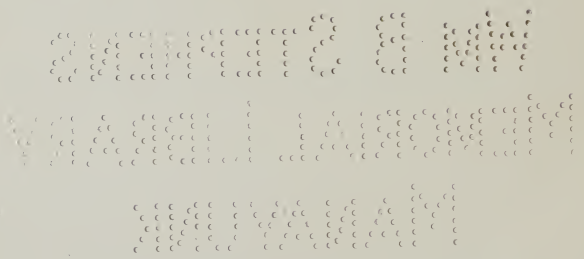

## TRANSLATORS' PREFACE.

ABRIDGMENTS of English waterproofing patents up to the last published in May, 1903, have been added to the original German work of 1897 in order to bring it up to date. It may be taken for granted that if a process is worth anything it is patented in England.

The author deals almost solely with the waterproofing of garments, and we have not gone outside this limit in our selection of patents.

LONDON, *September*, 1903.

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## CHAPTER I.

### INTRODUCTION.

Waterproof fabrics are those which, by covering over the fibres or the filling up of the interstices between them with a substance insoluble in water, are not only protected from the destructive effect of dew, rain, snow, etc., but protect objects which they cover from these atmospheric influences. The waterproofing is done with fats, oils, varnishes, pigments, guttapercha, indiarubber, and other media. Little has been written on the subject, and the few writers who have treated of the matter cannot be congratulated upon their efforts. It is customary to include under waterproofing such processes as the impregnation of wood and paper pulp, the manufacture of waxcloth, and of articles of indiarubber and guttapercha, etc. In my opinion, however, the term should be restricted to the treatment of woven fabrics by chemical means so as to precipitate insoluble oxides in the fibre, or the impregnation of the fibre with organic bodies, such as paraffin, wax, etc., so as to make it impervious.

Absolute impermeability can never be attained, and does not exist, even if the fabric has shown itself watertight for weeks or even months. If a pouch is made of a waterproof fabric, and kept full of water, we notice at last that the colour of the outside begins to change up to the level of the water inside, without the water itself showing. The outside often, too, begins to get mouldy. These appearances prove that the water has to some extent penetrated the fabric, and occur soonest if the waterproofing has been done with

aluminium acetate, as the basic alumina salts in the fibre gradually dissolve. There is no such thing as a substance absolutely insoluble in water.

Materials, when waterproofed by the chemical method, undergo changes only visible under the microscope. If we put an untreated fibre under the microscope, and then bring it into contact with a drop of water, we shall see it suck up the water greedily. But if it has been treated with alumina the water is not absorbed, and the drop looks like a pearl traversed by the dark threads. Many bubbles of air crowd round the separate threads and stick to them very obstinately, so that even hard pressure with the cover glass will not get rid of them. The behaviour of coloured fibres is different after they have been waterproofed with acetate of alumina or a metallic soap. Here we usually find both the dye as a lake and the metallic oxide adhering to the fibre. If, however, we waterproof with ammonium cuprate or other ammoniacal solutions of metals, we notice not only the deposit of metallic oxide but that the fibre has been altered and parchmentised.

A fabric to be waterproofed must be woven very close. It does not matter whether its material is animal or vegetable. By chemical impregnation the fibres are to be made to keep back the water mechanically, and the interstices between the threads should not be filled up. A very closely woven fabric is very impervious of itself, and will resist water as long as the fibre will take it up without passing it on. In waterproofing light, thin-fibred or wide-meshed fabrics, therefore, they have to be treated with an application which will fill up the interstices and afford protection as long as possible against outward agencies. This treatment, however, alters the whole fabric. The threads become stiffer, more brittle and less durable, while fabrics waterproofed by chemical means undergo no striking change.

It has been already mentioned that fabrics are water-

proofed by impregnating them with fats, such as linseed oil, boiled oil, etc., or made impervious by applications of india-rubber, varnish, resin, pitch, tar, pigments, etc. We shall not deal here with such methods, as they merely give a protective coating which protects from the weather exactly as wood and other constructive materials are protected. Our intention is to describe those processes which are usually called chemical, and also those which act by stopping up the cells and pores of the fabric with an easily deposited substance. In the former case, precipitates of insoluble metallic compounds or of insoluble metallic soaps are produced in and upon the fibre by chemical reactions. In the latter, the fibres are soaked with paraffin, wax, etc., in solution. The solvent quickly evaporates and leaves the paraffin, etc., behind in a state of very fine division. Both classes of process yield products in which the fabric has suffered no change visible to the naked eye, and the material, although waterproof, is pervious to air. According to the treatment the impermeability to water is limited or practically boundless, and the fabrics retain their original colour, softness and suppleness, except in a very few cases. For example, if tannin is used, the colour of the fabric becomes somewhat darker, but only an expert would notice the difference.

If a bleached or unbleached fabric is waterproofed with acetate of alumina, its appearance and "feel" remain exactly as at first. The following substances are used in particular for waterproofing fabrics: sulphate of alumina, alum, acetate of lead, the sulphates of copper, zinc and iron, ammonium cuprate, chromate of potash, paraffin, ceresine, wax, soap, etc.

## CHAPTER II.

### PRELIMINARY TREATMENT OF THE FABRIC.

The fabric to be waterproofed must, if unbleached, first be boiled with soda or lye, so as partly to remove the dye and grease in the fibre. Hemp, linen and jute fibres offer great resistance to taking up water, on account of their great content of fat. Half or entirely bleached fibres have the peculiarity that they are not very receptive of the waterproofing fluid, so that they, too, must be scoured as above. The scouring is best done with a 3 to 5 per cent. solution of carbonate of soda, either in large paraffined wooden vats, or, better, in iron boilers, which have been painted inside thickly with asphalt varnish (a solution of natural asphalt in benzine or oil of turpentine, mixed with some good copal varnish). The vessels must be large enough to take several pieces at once. Whether of wood or iron, they must always have a false, perforated bottom and a heating coïl of copper wire.

The soda (ammonia soda is the best) is dissolved in water and poured over the goods placed loosely tied up on the false bottom of the boiler. The lid, in which there is a pipe for the escape of steam, is then put on and the contents are boiled up. It is best not to use direct steam, and to make up the water as it evaporates. Condensed water, still hot, should be used for this purpose. After boiling for an hour or two, the steam is shut off, and the boiler left for about twelve hours. The dirty water is then run off, a cock being put below the false bottom for that purpose. It rarely pays to recover the soda from the dirty soda solution, although it

may be worth the while under very special local conditions.

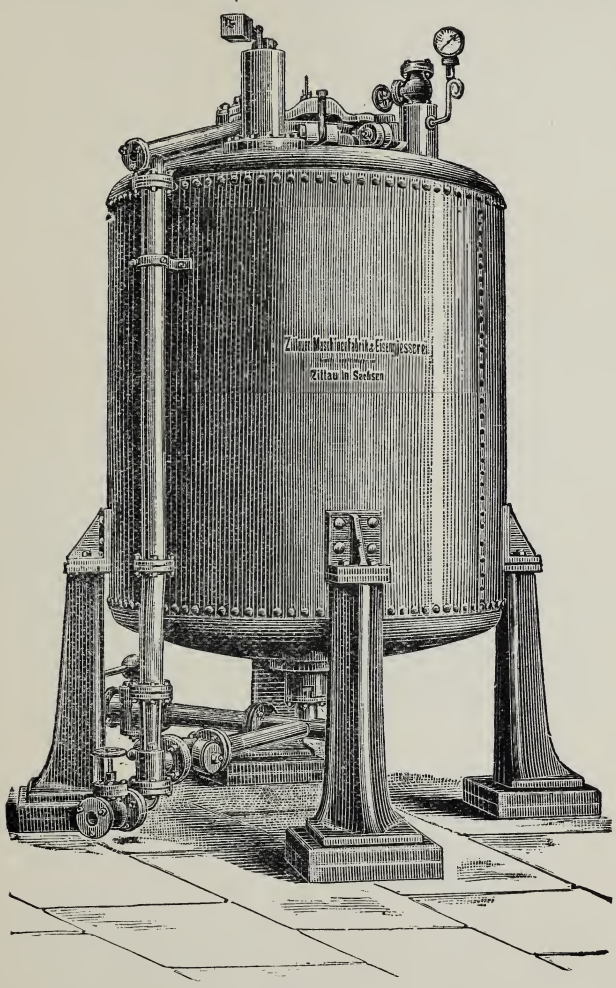



Fig. 1.

The above process is done quicker and better under pressure. Fig. 1 shows a high-pressure boiler of wrought iron, tested

to eight atmospheres pressure, and fitted with a manhole. In the centre a turbine is fitted, which, in rotating, pours the soda solution, made to flow through it by the action of a pump or injector, uniformly over the fabrics. The apparatus is heated by high-pressure steam. Fig. 2 shows a different system. The boiler resembles an ordinary kier. The fabric,

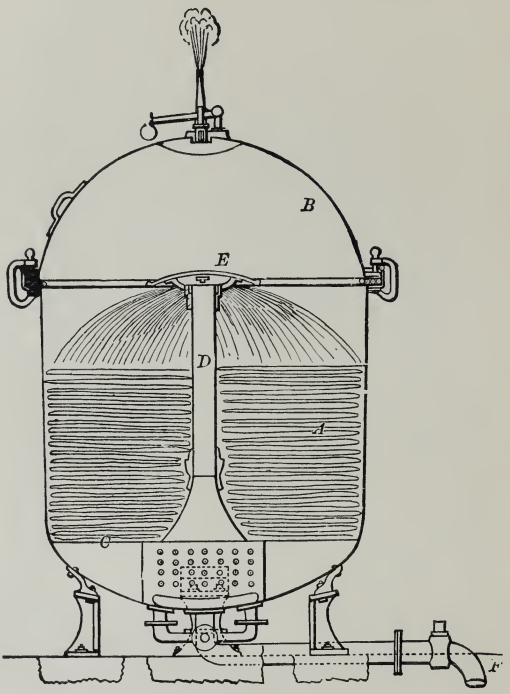



Fig. 2.

A, is piled on the false bottom, C. A tube, D, brings the soda solution from below, and it is discharged over the goods by E. The soda is forced up D by the pressure of the steam. This system acts intermittently, as after each outburst from E the pressure of the steam must increase, till it again overcomes the weight of the liquid in D.

When the goods are scoured in one of these boilers, clean water is run over them till the soda is completely rinsed out. This process can be hastened by acidifying the first wash-water with sulphuric or hydrochloric acid. Instead of scouring, the goods can be washed with a full-width washing machine (Fig. 3), with a divided wooden chest with rotating vanes in it. The washed and rinsed pieces are either hung up to dry, or centrifuged, or dried on a cylinder drying machine. A horizontal hydro-extractor, such as is shown

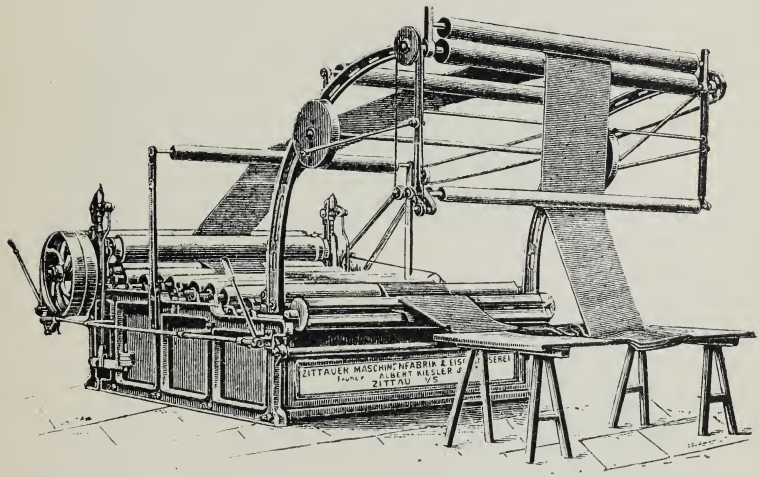



Fig. 3.

in Fig. 4, is the best, and in this the fabric is drawn on to a drum and then centrifuged. Another type is the full-width hydro-extractor shown in Fig. 5. This machine works quietly at a great number of revolutions, is easily accessible, and does not consume much power. Simpler and more effective, however, is the machine shown in Fig. 6. On a horizontal axis four boxes are arranged, which have bottoms and sides of strong iron rods. Each will hold one or two pieces of fabric. When they are all full, lids are put on them

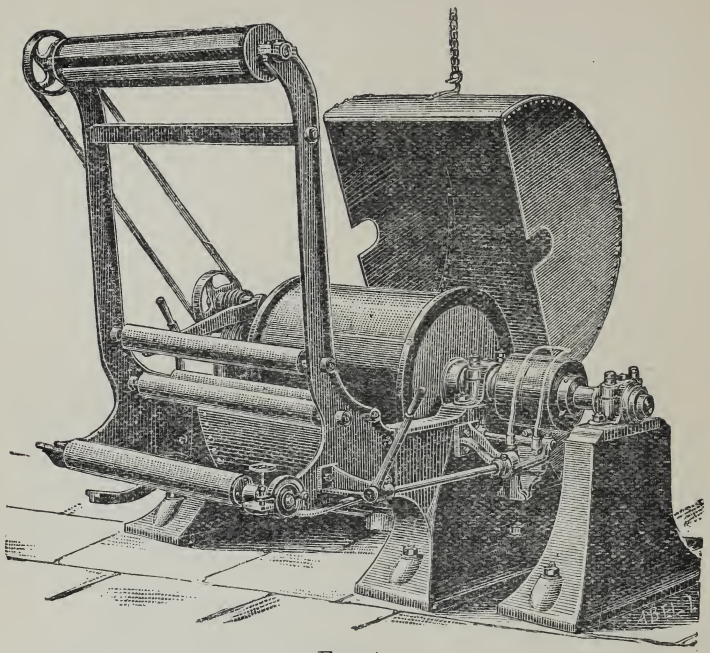


FIG. 4.

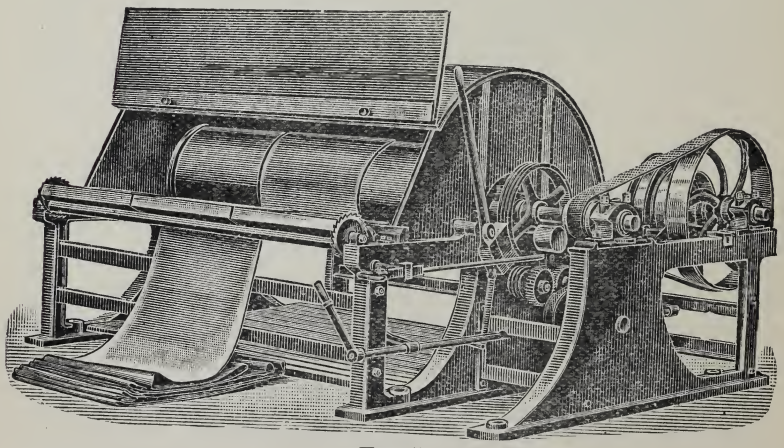


FIG. 5.

and the axis is rotated. Centrifuging in this way causes no creases.

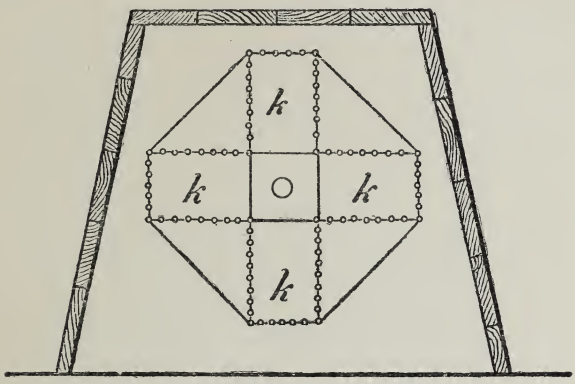



Fig. 6.

Cylinder drying machines (Fig. 7) are largely used. They consist of a varying number of hollow copper cylinders, and

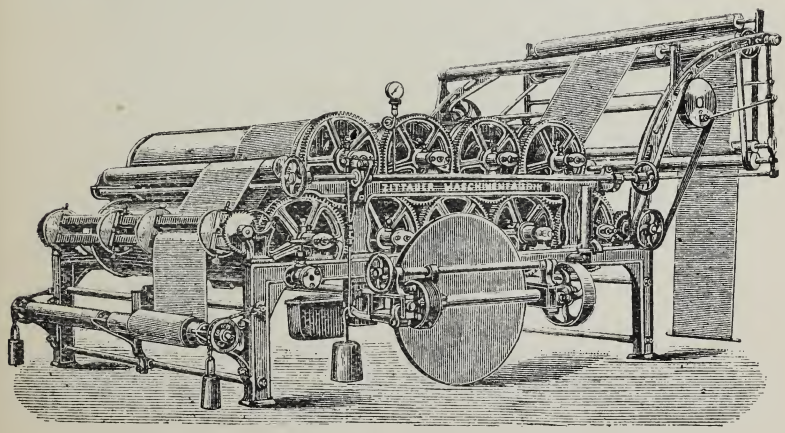


Fig. 7.

are heated by steam. The ends of the cylinders are made steam-tight, and they draw the fabric through the machine

by friction. Gear is provided for regulating the speed. The machine is provided with stretching frame and cylinders for receiving the dried goods. In machines with two rows of cylinders, both sides of the goods come into contact with the hot cylinders. Care must be taken that the diameter of the cylinders is not too great. It should not exceed 570 millimetres, as repeated experience has shown that small cylinders are much to be preferred to larger ones. This is easily understood if we compare the useful surface with the useless, *i.e.*, the curved surface with the surface of the cylinder ends. If we compare one cylinder of 3 metres diameter with three each of 1 metre, we get the same result for the total circumference in both cases, *viz.*, 9·42 metres. But the ends of the 3 metre cylinder have a total area of $2 \times \frac{9}{4} \times 3{\cdot}14 = 14{\cdot}13$ square metres, and the total area of the six ends of the 3 metre cylinders is $6 \times \frac{1}{4} \times 3{\cdot}14 = 4{\cdot}71$ square metres only. Hence the surface which has no drying action, and which wastes heat by radiation, is much smaller in the case of the small cylinders, while the useful surface is the same. Besides, having a large number of cylinders permits a more gradual raising of the temperature than is possible with only a few cylinders. Small cylinders, too, are more easily removed and replaced than big ones.

Another advantage with smaller cylinders is that the goods pass more quickly from cylinder to cylinder, and there is much less risk of the goods clinging to the cylinders than with large cylinders. The different cylinders must all be of the same diameter, and be turned quite true so that the fabric will travel uniformly. The foundations of the machine must be solid. The steam enters the cylinders through their hollow axes, and condensed water is run off in the same way. The bearings may be connected with the steam-tight cylinders, without any packing, by a system of exactly turned wrought iron rings. To get the full efficiency of the machine, all water that condenses in the cylinders must

be at once got rid of. The Hanbold arrangement fixed to each end of the cylinder for this is excellent. The lifting tubes often used have the disadvantage that they only remove the condensed water partially, and not at all if the steam pressure falls below a certain amount. Empties bolted or soldered to the cylinder case are no better. If they are bolted, the bolts become loose, and the fabric gets

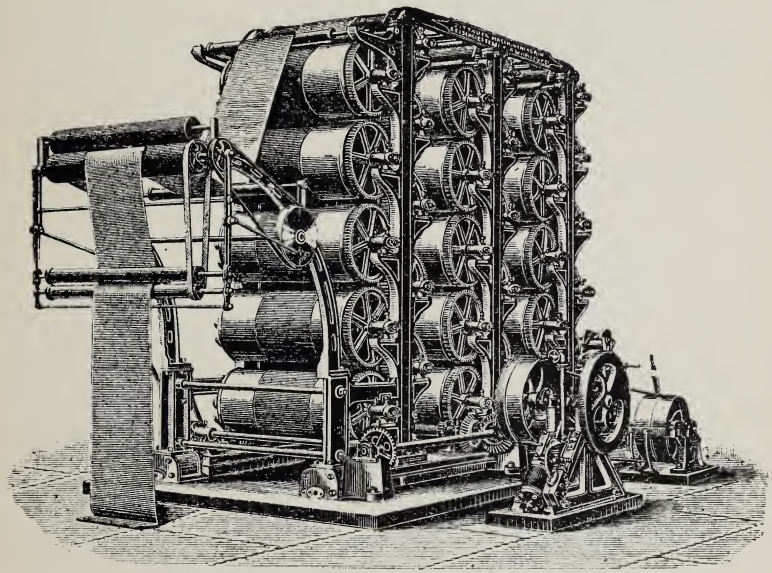


Fig. 8.

wet stains, while if they are soldered, the solder soon gives out, and the arrangement ceases to act. To protect the cylinders from collapsing by the production of a vacuum in them, it is not sufficient to have simple air valves in the cylinder ends. There should be an air valve also over the cylinder bearings. Where there is lack of room, upright drying machines should be used. A very compact power

drier of this type, with thirty cylinders, is shown in Fig. 8. The construction is evident without verbal explanation.

The drying of the fabrics on these machines demands great care in maintaining an equable temperature. The copper cylinders, too, must be kept scrupulously clean, or the fabric will he marked by them with stains which will not take the waterproofing liquid properly and will show in the finished goods. My experience is that it is best of all to dry in a full-width hydro-extractor, which turns out the fabric ready for waterproofing.

## CHAPTER III.

### WATERPROOFING WITH ACETATE OF ALUMINA.

As an impregnating fluid acetate of alumina has great advantages. It is prepared by the waterproofer himself, and any one of the following methods of preparation may be employed :—

1. Decomposing sulphate of alumina with acetic acid in the presence of chalk.
2. Decomposing sulphate of alumina with sugar of lead.
3. Decomposing sulphate of alumina with acetate of lime.

Alum can be used instead of sulphate of alumina, but the latter is generally preferred, not only because it is cheaper, but because it comes on the market free from iron, or practically so. Freedom from iron is very important, especially if the fabrics have to be soaped in the waterproofing process.

Method number one is worked as follows : Dissolve 30 lb. of sulphate of alumina in 8 gals. of cold water. Then add 36 lb. of 30 per cent. acetic acid (sp. gr. 1·041). Then stir in, a little at a time, a paste consisting of 13 lb. of levigated chalk and 2 gals. of cold water. The equation is : $Al_2(SO_4)_3 + 5H_2O + 3CaCO_3 + 4H_4C_2O_2 = 3CaSO_4(H_2O)_2 + Al_2(HO)_2(C_2H_3O_2)_4 + 3CO_2$.

The reaction, however, is not really so simple. No heat must on any account be used. On account of the evolution of carbonic acid, the vessel must only be about two-thirds filled. It must be provided with a stirring gear, not only to keep the chalk from sinking down but to get a uniform product. The chalk must be put in through a fine sieve to

keep back sand and dirt. When all the chalk is in, keep the stirrer going for five or six hours, and then allow the mass to stand. As the decomposition is not quite complete even after twenty-four hours, the stirrer should be worked again for another six hours at the expiration of that time, and the mass is then run off into a settling cask. After twenty-four hours in this, the solution of acetate of alumina can be drawn off from the precipitate of sulphate of lime. It is better, however, to effect the separation by centrifuging or by a filter press.

A filter press consists of a series of filtering chambers, separated by solid partitions. They are included between two strong end pieces, one of which is fixed, the other movable. Filter cloths are put between the partitions, and must be large enough to prevent leakage at the edges. By means of levers, screws or hydraulic pressure, the whole contrivance is pressed into a single close mass, and we get a number of adjacent vacant spaces communicating with one another by openings, and into which the liquid to be filtered is pumped, or enters by its own weight. During this it is separated from solid matters, as it passes through the cloths and runs off by special canals, while the solid matter remains in the filter press.

According to whether the mass to be filtered enters in the middle or at the sides, and the space for the cakes is formed by the projecting edges of each pair of plates, whereby the cakes fall out freely when the filter press is opened, or the space for the cakes is formed by frames hung alternately with the filter plates, so that they can be lifted out with the cakes in them, filter presses are classified as chamber presses and frame presses. Chamber presses have the advantage that they are of stronger build, and hence more durable. Two filter cloths are always in contact, so that they make a tight joint, and, as the opening in the centre of the chamber for the entrance of the stuff to be filtered is made large, there

is no fear of the apparatus becoming choked. They have, however, the disadvantage that the filling of them with cloths takes a good deal of time; even if the cloths have been prepared by the best methods, the cakes have a hole in the middle instead of being entire.

Frame presses have the advantage that they take less filter cloth, as each chamber is made tight by a single cloth. The cloths must not be stretched, and the cakes remain whole. Their disadvantage is that, on account of the smallness of the

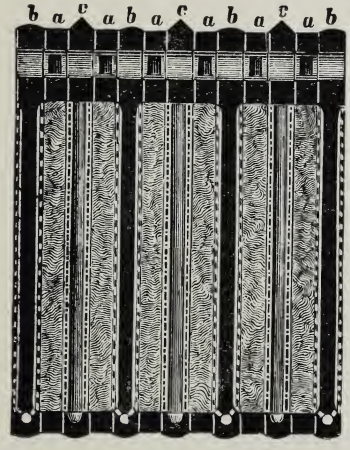



Fig. 9.

channels in their frames, they easily get choked, so that single chambers remain empty. After every operation the frames have to be carefully scraped and cleaned, that everything may be tight for the next time the press is used.

Besides the above systems, we have the three-chamber filter press, distinguished from the others by having no cloths, and containing instead layers of sand or charcoal. This press gives a specially clear filtrate. Fig. 9 shows the arrangement of the plates. Between every pair of frames, *a*, is a plate, *c*, while outside the frames the plates, *b*, are placed. The plates

*b* and *c* serve to carry off the filtrate. The sand or charcoal is put into the frames, *a*, from above, and forms a solid cake from which the filtrate passes to the channels in *b* and *c*. When the frames, *a*, have thus been filled with filtering materials, the plates, *c*, are removed and replaced by the frames, *d* (Fig. 10). The frames, *a*, and the plates, *b*, are not removed.

As the filter cakes must be freed from the filtrate that clings to them, a rinsing arrangement must be attached to a filter

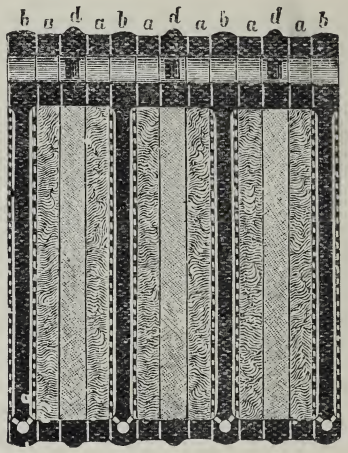



Fig. 10.

press. For this purpose, two additional channels are provided in each filter plate—one to admit the rinsing water, the other for its escape. The first channel is connected with the filtering surface of every other plate only, whose draw-off cocks are shut, and admits water behind the cloths, and therefore behind the cakes. It goes through the first cloth and then through the cakes, then through the second cloth, and runs at the back of the latter away through the second channel, taking with it the liquid rinsed out of the cakes,

The cakes are rinsed till all the acetate of alumina has been got out of them. Everything coming from the press which is not of lower gravity than 3° B. is used in waterproofing, and the weaker liquors are employed to dissolve the next lot of sulphate of alumina and to mix the chalk with instead of water. The cakes of gypsum left in the press have no value, and are thrown away. The filter press is to be preferred to the hydro-extractor, as it gives a clearer filtrate and does not require such skilled and careful attention.

A variation in the process described consists in stirring together 36 lb. of 30 per cent. acetic acid, 13 lb. of levigated chalk, and 2 gals. of cold water, till the evolution of carbonic acid has nearly ceased. The mass is then left for a few hours, when a solution of 30 lb. of alumina sulphate in 8 gals. of water is poured in. After stirring till the fresh evolution of carbonic acid has ceased, proceed as before directed.

It will be seen that this method of preparing acetate of alumina takes a long time, and is, on account of the use of acetic acid, rather expensive. The acetate of alumina obtained contains some undecomposed sulphate, but that is no bar to the use of the solution and does no harm. A considerable number of people consider that the best acetate of alumina for waterproofing is that prepared by the reaction between sulphate of alumina and acetate of lead. The proportions of the two to be taken are stated differently by the various authorities, as some take equal weights, some more acetate than sulphate, and some more sulphate than acetate. At all events cold solutions only must be used, and a mechanical stirrer is indispensable for proper work. Besides the mixing vessel with its stirrer, two smaller vessels are required, one for dissolving the lead salt and the other the sulphate of alumina. These vessels are placed above the mixing vessel so that their contents can be run into it by taps. They are tilted so that the taps are at their lowest parts, and they can be completely emptied. The liquids are led into the mixing vessel by funnels closed by

wire gauze for filtering purposes, and flowing together into the larger vessel. Water having been previously put therein, the stirrer is set in motion and the cocks are opened to let in the two solutions. When all is in, the stirrer is kept at work for about six hours. The liquid is run off into the settling cask and left for twenty-four hours to clear. The clear solution is then run off, and the precipitate is washed on filter cloths, or the whole is pumped directly into the filter press, which is afterwards rinsed out in cold water. Here, too, the liquors of not less than 3° B. are used in waterproofing and the weaker ones used for dissolving fresh lots of lead and alumina salt. This process, too, is not very cheap, on account of the price of sugar of lead. The bye-product (sulphate of lead) certainly has some value, but only as a pigment, for which purpose it is very inferior in body to white lead. The conversion of sulphate of lead into white lead entails a good deal of labour and expense.

As equally good acetate of alumina to that obtained as above can be got by cheaper methods, the foregoing processes should not be used except in case of necessity. When prepared by the second method, the acetate of alumina should contain an excess either of sugar of lead or of sulphate of alumina. This is of no consequence provided the waterproofing process includes a soaping, for in this case the excess is converted into insoluble soaps. If, however, the goods are not soaped, the solubility of the salt in excess detracts from the waterproofness. Fabrics containing an excess of sugar of lead acquire a blackish-grey appearance in air containing sulphuretted hydrogen, on account of the formation of sulphide of lead.

Unquestionably the cheapest method of manufacturing acetate of alumina is to use sulphate of alumina and crude acetate of lime. The process is exactly like that above described with sugar of lead. The crude acetate of lime has a grey, sometimes nearly black colour, owing to the presence

in it of tarry matters. The larger the proportion present of these the darker is the colour. Too tarry an acetate should not be used, as it gives a very dark solution of acetate of alumina which is not easily decolorised. The crude acetate of lime always contains carbonate of lime as well, and it is necessary to find out by trial how much of it is required to react with a given weight of sulphate of alumina. It is a good plan to keep solutions of both the ingredients in stock, ready for mixing in the proper proportions. The apparatus necessary is the same as when sugar of lead is used.

The most usual proportions are 100 lb. of crude calcium acetate to 700 lb. sulphate of alumina, dissolved separately in water to a strength of 5° to 8° B. It is necessary to have plenty of room in the mixing vessel, to provide for the evolution of carbonic acid. When the evolution of gas has ceased, a sample of the mixed fluids should be taken, and part of it tested with chloride of barium, and part with sulphuric acid or with oxalate of ammonia. If the barium chloride gives a precipitate the sulphate of alumina is in excess, and if the other reagent gives a precipitate there is too much acetate of lime, so that after the test matters can be put right by adding more of whichever salt is deficient. This should be repeated till a precipitate is given in neither case. We then have an acetate of alumina which contains no more than traces of an excess of either ingredient. It is better to have an excess of sulphate of alumina than of acetate of lime. A small excess of the former does no harm, but an overplus of the latter is to be avoided.

As in the other processes, the solution is run off and filtered through cloths or a filter press as already described. The cakes of sulphate of lime from the press can be used with lime and ashes for mending roads. The acetate of alumina solution is generally used of a strength of from 3° to 5° B., but often from 6° to 8° B. It must be clear and give

no colour with sulphuretted hydrogen. A white precipitate with that reagent shows the presence of zinc, a dark coloration the presence of lead or copper. If 5 cubic centimetres of the solution are mixed with 10 cubic centimetres of 90 per cent. spirit, there must be no precipitate, but only an opalescence.

## CHAPTER IV.

### IMPREGNATION OF THE FABRIC.

The simplest, most primitive, and least to be recommended method of doing this is to leave the prepared fabric lying for twelve hours in the acetate of alumina solution. This method, if work is done on anything like a large scale, requires much space and labour and a large number of vessels, besides a large stock of acetate of alumina, as the pieces must be entirely immersed. As the pieces lie folded in the liquid, the outer parts of them absorb more than the inner, so that the impregnation is very far from being uniform. The consequence is that the fabric has to be treated with the acetate a second time. These difficulties can be avoided by using the sinker shown in Fig. 11. The fabric is there stretched on a frame provided with hooks. The frame consists of a vertical rod with a hook on it above and below. It carries a system of radial and concentric rods at each end. The lower system is fixed, but the upper can be raised or lowered at will. Both are liberally provided with hooks for stretching the fabric. The end of the piece is fixed in the middle, and the length is wound round and round the apparatus, so that the piece is hung up at full width. When the piece has been fixed the upper system of rods is raised so as to stretch it. The whole is then suspended by a chain in the impregnating liquid, which must be heated to 35° or 38° C.

It is very difficult to heat a large mass of liquid uniformly. In this case it is impossible to use direct steam, for if the

temperature rises above 38° C. the solution is precipitated in the form of a basic acetate of alumina and becomes useless.

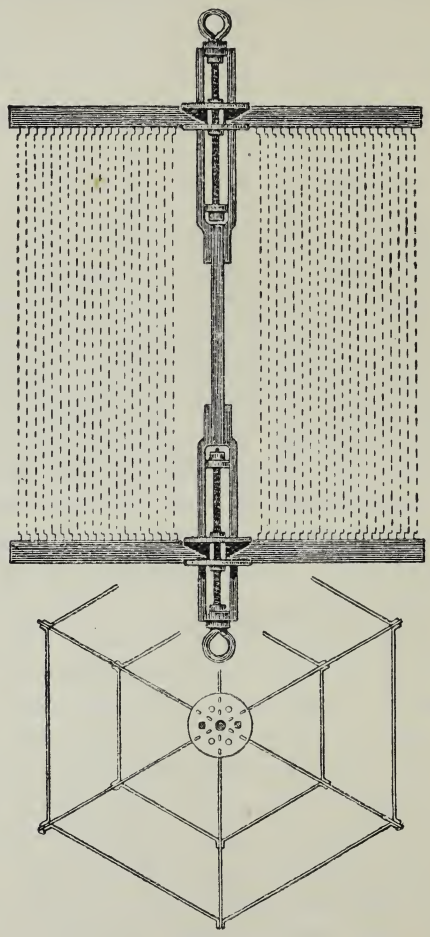


FIG. 11.

This precipitation takes place at once where the steam enters, and soon covers the perforated coil. Again, it is impossible to maintain a uniform temperature by stirring, as there is too

large a bulk of fabric in the liquid. The lower part of the liquid is apt to become precipitated, as above stated, while the upper part remains unheated, and it is well to heat the aluminium acetate, even in the summer, while in winter it is a necessity. Many people try to avoid the difficulty by giving the fabrics twenty-four or even forty-eight hours in the solution, so as to give the heat every chance of becoming uniformly distributed. This, however, is not advisable, for some of the dye left by the preliminary scouring then gets into the liquid and renders it unsuitable for further use. Whether this long sojourn in the acetate tenders the fibre or not is not yet certain. Experiments with a view to ascertain this are being carried on, but have not yet been concluded. The impregnation need not take longer than six hours, or eight at the outside, and when it is finished the liquid is run off by means of a cock placed at the lowest part of the vessel below the false bottom. It is then pumped into another impregnating vat for use over again. The fabric is left for a time on the false bottom to drain. During this time the pieces are turned over once, to prevent one part of them from being wetter than another. If the sinker has been used it is turned upside down after partial draining, and the framework is continually rotated.

It is, however, in all cases better to effect the impregnation by mechanical contrivances. The jigger, the padding machine, and the roller printing machine, can all be made to do excellent service in this way. Their use is the more to be recommended as they effect a great saving of impregnating liquid. The pieces are sewn together at the ends, and wound up either by hand or power upon a reel. It has proved advantageous to make these machines with semi-cylindrical floors, and to allow the upper parts of the sides to separate far enough for the liquid driven out from the fabrics by the wringing to fall back into the box. At the bottom of the box is placed a steam coil for

heating the liquid, or, better, the box is provided with a steam jacket for the purpose. A cock serves for emptying the box, which is made of deal or of iron, and lined with copper or indiarubber. At various depths within the box guiding rollers are placed, usually from two to five, in the liquid near the bottom, and the same number near the edge

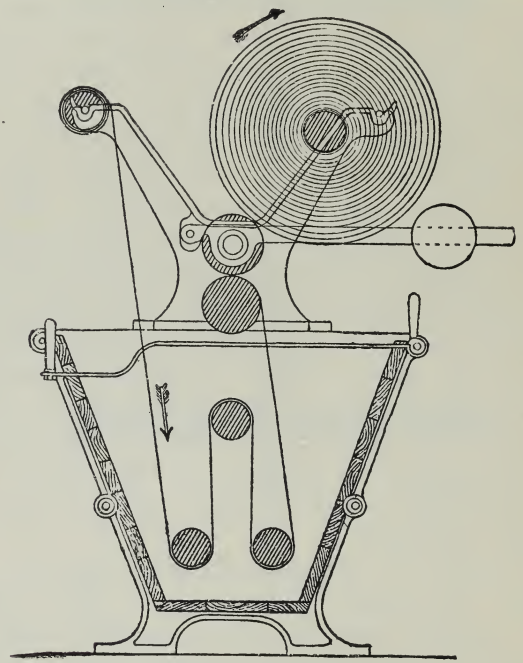


Fig. 12.

of the box and outside the liquid. There is also a pair of wringing rollers. The guiding rollers are of wood. The wringers are covered with indiarubber. The reels for the fabric are capable of having their rotation reversed, so that the cloth can be passed backwards and forwards through the impregnating liquid. A brake is used with the winding-off reel to give a certain amount of tension to the cloth. The

arrangement of this jigger is shown in section in Fig. 12. A fabric runs full width under the guiding rollers in the liquid, then through the wringers, and then on to the receiving reel, and goes backwards and forwards till its whole length is properly impregnated.

If we use a padding machine instead of the jigger, the stuff is wound off one roller, passes over guiding rods, and is spread out flat by a spreader. It then enters the trough containing the impregnating liquid. At the bottom of the trough are two or three wooden rollers and a copper steam

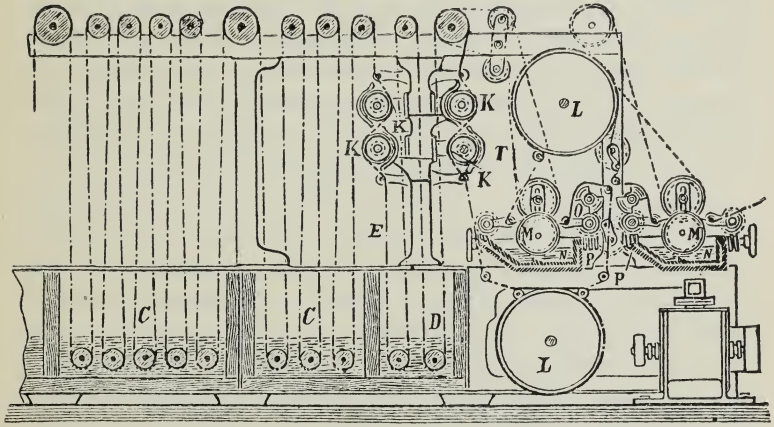



Fig. 13.

coil. From the trough the fabric passes through a pair of indiarubber wringing rollers, and is then rolled up. As the entry and exit of the fabric are at the same side, the machine must be built extra high, so that it is possible to work the goods under it. The writer has seen in one factory a full-width washing machine used for impregnating, it being provided with reversing gear.

A somewhat different apparatus is that of Miller & Son (Fig. 13). This consists of a number of vats, C and D, containing the impregnating liquid, and ribbed and perforated

stretchers, K, from the inside of which the air can be exhausted, as well as of heated cylinders, L, and one or more rollers, M, dipping into the trough, N. N is filled with hot substances soluble in water, through which the fabric travels.

Whatever kind of apparatus is used, care must be taken to keep a proper quantity of impregnating liquid in the troughs, pouring more in as it is removed by the fabric; the specific gravity of the liquid in the troughs must be tested from time to time and reinforced if it has become too dilute. The fabric is passed backwards and forwards through the liquid for four to five hours, at the end of which time it will have become thoroughly soaked. The most rational and rapid, and the cheapest, method of impregnating is by means of a vacuum. The necessary apparatus occupies very little room, requires little labour, and only small quantities of impregnating liquid, while the action is mechanical throughout.

The apparatus is a cylinder made of iron or wood, and lined inside with thin sheet copper. The cover is removable, and with it a basket composed of thickly coppered iron rods, and having a smaller diameter than the cylinder itself, can be lifted in and out. The cylinder can stand upright or lie on its side, according to the space available. The basket is divided into compartments by gratings or perforated plates, so that several lots of fabric can be impregnated at a time. The fabrics are wound up into loose rolls which are stood on end. The cylinder is provided with the necessary accessories for heating it, exhausting the air from it, etc., as well as cocks for admitting and removing liquid. The dimensions of the cylinder are so adjusted that very little liquid is needed to fill it. When the cage is filled with fabric and a vacuum has been made, the impregnating liquid is admitted into the cylinder. When it is full, as indicated by the gauge glasses provided, more is forced in by a pump, until there is a pressure of $2\frac{1}{2}$ to 3 atmospheres inside the cylinder. This pressure is kept steady for from 30 to 45 minutes. The air

and blow-off cocks are then opened, so as to drain off the liquid. This, after having been reinforced to the proper strength, is pumped back to the cylinder for a fresh operation. When the liquid has run out, the cover is removed and the basket is taken out. A fresh basket full of fabric has been got ready during the treatment of the first batch, so that it can be put at once into the cylinder, and the work can go on as nearly as possible without interruption. Mechanical arrangements, such as systems of levers, etc., are provided for this manipulation.

The process secures complete penetration of the fibre by the solution of acetate of alumina. The exhaustion of the air between the fibres and from the interior of the cells of the fabric gives the liquid free access to every part, so that every cell gets filled with it. This is, of course, also facilitated by the pressure put upon the liquid as above described.

## CHAPTER V.

### DRYING.

After the fabric has been impregnated by one of the above methods, and has been drained of excess liquor as far as possible, it has to be dried. This process must be done at a high temperature, so as to ensure the formation of the insoluble basic acetate of alumina and to fix it in the fibre. During this reaction acetic acid is evolved and makes itself evident by its smell. The drying rooms are usually brick chambers, and must be roomy, so that the workpeople can move about in them freely in putting in and removing fabrics. They must also be provided with regulated inlets and outlets for hot, cold and damp air. Every opening, including the doorways, must be closed by well-fitting doors, which should be bad conductors of heat. It is a good plan to have hollow iron doors filled with asbestos alum. The windows should have closely fitting iron shutters, by the closing of which any conflagration can be checked. The drying house should be divided into compartments separated by passages, and it is necessary to provide water and steam pipes inside, so that either water or steam is available in case of fire.

The use of wood must be avoided wherever possible in the construction of the drying house, and what is used should be soaked in waterglass. Iron is to be preferred in building, and both the metal and the wood should be covered with several coats of good cement. The roof should be of concrete, sloping to each side from a ridge. The concrete should be

covered externally with a smooth layer of cement. Such a roof is suitable even for the coldest places, and its smooth surface is easily kept free from snow. It is an excellent plan to have a space, closed air-tight, between the roof and the ceilings of the drying rooms. This space keeps the ceilings always uniformly warm, because the confined and warm air above them interposes between them and the cold roof.

If the drying rooms are to dry the fabrics hung up in them quickly and completely, there must not only be a sufficient supply of hot air, but the damp air which has extracted the moisture from the fabrics must find a ready exit. This is best secured by keeping a slight vacuum in the drying rooms whereby the moist air is drawn out. The expense of this, however, would be too great, and we must confine ourselves to so constructing the drying rooms that the air in them rapidly changes. This may be effected by means of a chimney stack of sufficient height or by means of a fan if such a chimney does not exist. Even a fan will not always act as efficiently as desired if the rooms are at a temperature below 100° C., as is usually the case.

The usual arrangement is to heat the air in the rooms by steam or hot combustion gases, and to provide for the entry of fresh air at one place as fast as the hot air escapes at another. As the air always tends to travel to the fan or to the chimney by the shortest cut, there are clearly marked tracks where the drying is rapid, and other places where the air does not get changed so quickly and the drying is consequently slower or even stops altogether, as the stagnant air becomes too saturated with water vapour to exert any drying action. This is prevented, and a lively and rapid change of air is produced, not by sucking out the damp air, but by forcing it out by fresh supplies of hot air. The air is warmed in any convenient manner and forced in by a blowing engine.

A very suitable arrangement of a drying room is to have

a heating apparatus outside, behind which the heating surfaces lie in long channels, and consist of ribbed cast-iron

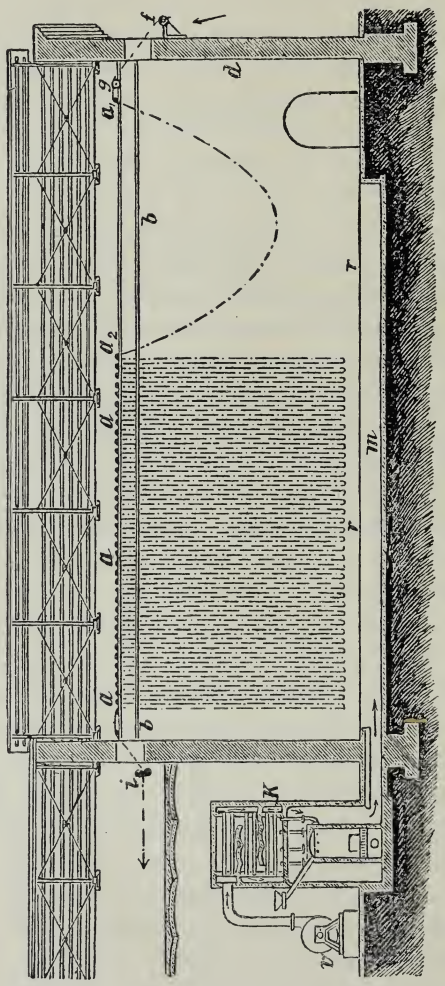



Fig. 14.

pipes round which plays the air from the blowing engine. The heated air then passes through shafts into the drying

room, which it enters in a very large number of places through slotted iron pipes. It is a very good plan to introduce the air below the floor of the drying room, and to let it enter through slits made all over the floor, as in Fig. 14. The damp air escapes by chimney-like shafts which lead through the roof into the open air, or, as it is still very hot, it can be led away for further heating purposes elsewhere.

As regards the arrangements inside the drying room for hanging up the fabrics, a proper frame must be provided,

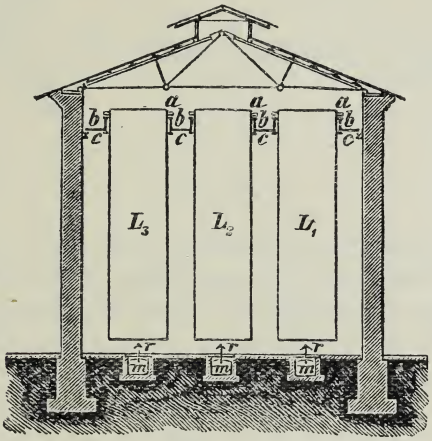



Fig. 15.

so that the fabrics may hang in numerous folds from ceiling to floor, so that the warm air entering may be able to pass over the vertical surfaces and dry them. Figs. 15 and 16 show such an arrangement where the fabrics are brought in from the side. The carrying rods, *a*, are carried by pairs of iron girders, *b*, which run parallel to the length of the room. Between every two pairs of girders is a board, *c*, for the workmen to walk upon when putting in or removing fabrics. The fabrics are brought in at one gable wall, *d* (Fig. 14), and when dry leave at the opposite wall. The two walls are provided

for the purpose with as many slits as there are rows of goods in the breadth of the drying room. Rails can be put outside the gable wall, *d*, for removing the rolls of dried fabric. The fabric enters the house guided by the rollers, *f*, *g*, and the

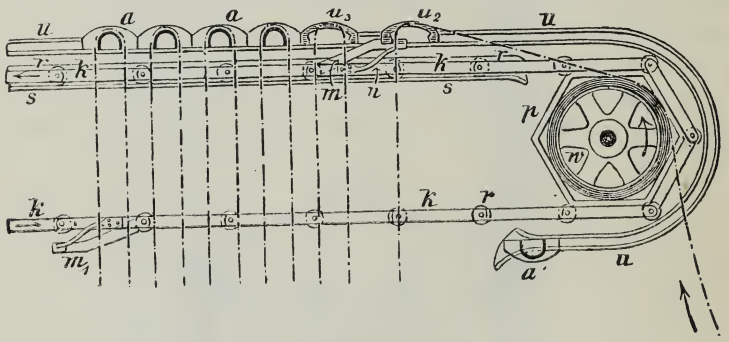



Fig. 16.

workman in attendance distributes them over the rods, $a_1$, $a_2$, so that the folds hang the full height of the room, pushing back each rod as he hangs the cloth over it, and so on until the room is full. The rods, $a_1$, $a_2$, are either wooden

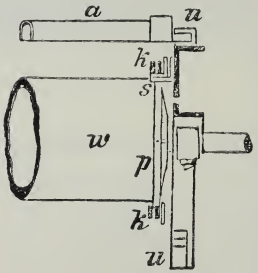



Fig. 17.

cylinders with square bearings, whereby they rest safely on the girders, or may be iron tubes fitted with similar bearings.

To save labour a feeding apparatus can be used. This is shown in Figs. 16 and 17. At the ends of the rows are

placed hexagonal wheels, $h$, over which pass the endless chains, $k$, which run on rollers, $r$, on the rails, $s$. At intervals equal to twice the length taken up by one fold of the piece, the chains carry the catches, $m$, lifted by springs, $n$. The iron carrying rods, $a$, end in cylindrical bearings, which rest in U-shaped rails, $u$, which pass round the hexagonal wheels, $h$, and then follow the rails, $s$. The fabric to be dried is drawn in by the aid of hollow wooden rollers, $w$, placed between each pair of chain wheels. A carrying rod, $a$, is then laid in the furrow, $n$, and then seized by the nearest catch, $m$, and pushed forwards in the furrow. This draws the fabric off the roller and forms another hanging fold. If at the end of the fold-forming the carrying rod, $a_2$, comes to the previously inserted rod, $a_3$, as shown in Fig. 16, the catch on the end of the chain is pressed down by the end of the rod, $a_3$, so that it releases the rod, $a_2$, and proceeds alone. The rod, $a_2$, on the other hand, remains where it was until it is pushed forward by the following catch, bringing another carrying rod and forming a new fold of the fabric, until it comes into contact with the rod, $a_3$. When the drying is finished, the fabric is removed from the drying house by two carrying rollers, $i$ (Fig. 14), and rolled up by a machine consisting of two guiding rollers and one on to which the fabric is wrapped.

The heating of the drying house is effected by a stove, shown in Fig. 14. A fan blows air through the stove when it is heated, and escapes by the cast-iron gratings, $r$, covering the channels, $m$, into the drying room. The hang of the cloth, *i.e.*, the height of the vertical sides of the folds, varies in different factories from 20 feet to 40 feet. According to the hang decided on, the dimensions of the drying house must be arranged. There must be a clear space of about 18 inches next the floor, and sufficient room above the drying fabrics for the workpeople to move about. Drying houses, it will easily be seen, take up a good deal of room, and

where the necessary space cannot be provided they must be replaced by drying machines. In these the goods are stretched in the usual way by endless chains provided with hooks, and so arranged that they can be run parallel to each other at any desired distance apart. They gradually bring back the fabric, contracted by the impregnation, to its original width.

The machines dry by means of hot air. Air is driven by a fan, first through tubes heated by ordinary or exhaust steam for the purpose of raising its temperature and then between two neighbouring horizontal stretched surfaces of fabric. In this way we get a quick drying very favourable to the appearance of goods impregnated with acetate of alumina. The machine is to be provided with automatic means of fixing and unfixing the fabric between the chains, automatic chain-stretching, and an arrangement for adjusting the position of the side walls by a worm-gearing, for keeping an exactly uniform width. The width between the chains and the speed of the machine are regulated at will, as well as the temperature of the air. Variations in speed are got by friction gearing, by which a very steady motion is imparted to the machine.

Drying machines are divided into those of one, two, three or four storeys, according to the number of times the chain passes over itself. Then, according to its size, the machine is divided by a number of vertical partitions. The first of the chambers so made is outside the drying room proper and only contains the apparatus for running the chain, and the apparatus is so arranged in it that in that chamber the chains diverge so as to stretch out the cloth to full width gradually. Figs. 18 and 19 show a several-storeyed drying machine. It consists essentially of connected, pillar-like stands, between which are arranged the rails carrying the chains. These rails are attached to the walls of the drying room, and screws are provided for regulating their gauge. The air is blown

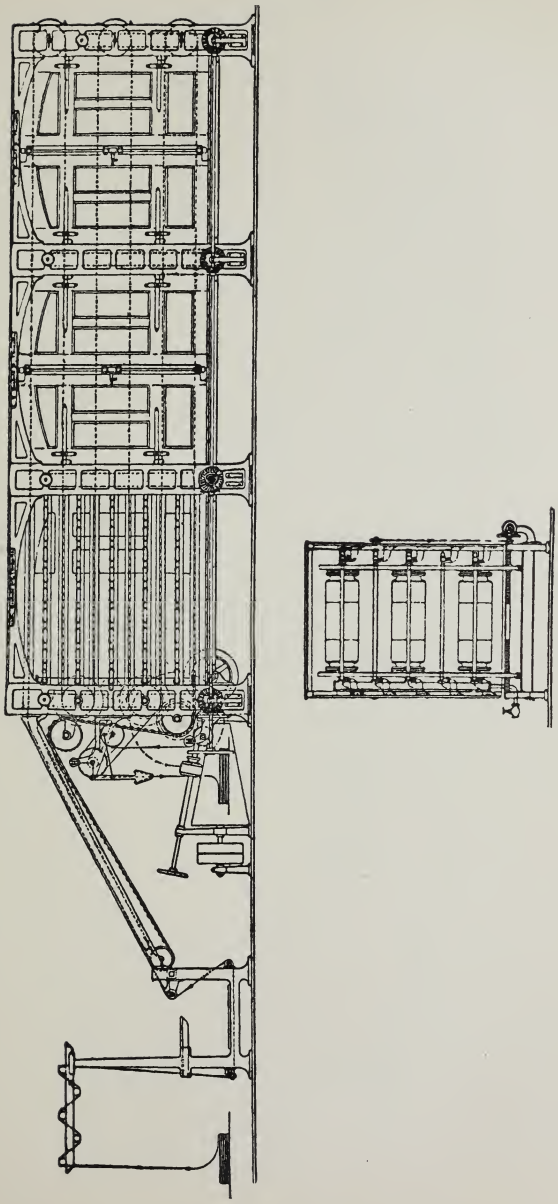


FIG. 18.

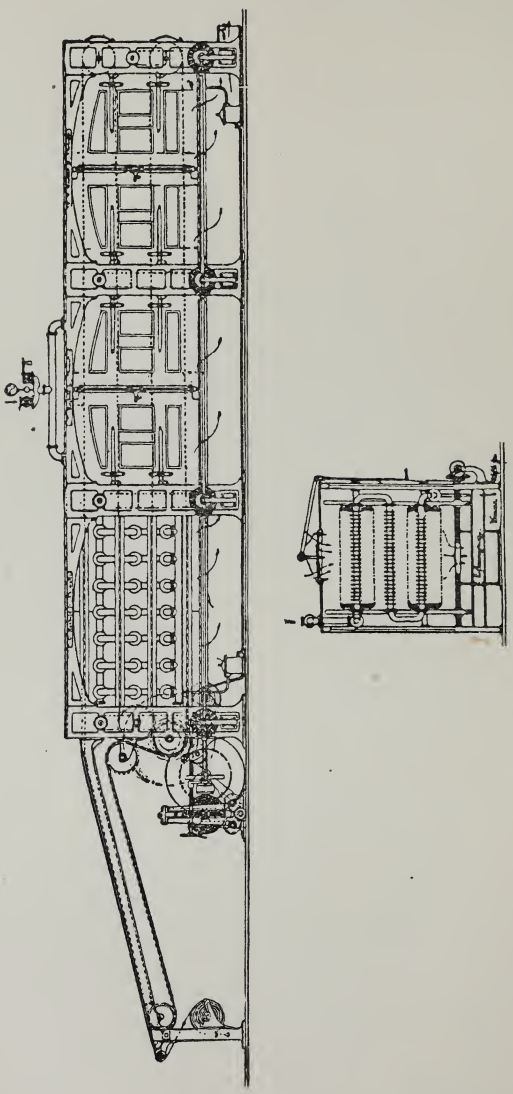


FIG. 19.

into the drying chambers from the heating arrangement above mentioned. As the illustrations show, these machines have been modified in points of detail. They are provided with other heating apparatus, ribbed tubes and coils, so as to get great drying action with economy of steam and power by the choice of suitable heating surfaces and volumes of air.

Cylinder drying machines have been already described and are a less effective form of apparatus. The disadvantage of them is that undyed fabrics, however clean they may be, come out streaky and dirty, probably on account of the action of the acetic acid on the copper cylinders.

The complete drying of the fabrics makes them waterproof from the formation in them of the insoluble basic acetate of alumina. Hence this very often finishes the work, and especially in those cases when it is specified by the customer that the fabric is to be so delivered. A fabric waterproofed in this fashion should show no damp places on the outside after having been made into a pouch and kept full of water for several weeks. If, however, we want absolute waterproofness, we must soap the goods in a 5 per cent. soap solution. The best soap solution to use is got by dissolving a neutral milling soap in soft water. If the water contains lime, the solution becomes turbid from the formation of lime soaps. If hard water must be used, it should be softened before the soap is dissolved in it, by adding the necessary amount of acetic or hydrochloric acid, found from a previous determination of the hardness of the water. Condensed waters should be used for dissolving the soap. The soap is dissolved in a small quantity of water by boiling in a steam-jacketed pan. The solution is then diluted to 5 per cent. strength. The solution must be yellowish and perfectly clear. It is advisable to filter it or strain it through a sieve to free it from all suspended particles.

The fabric, which must be quite free from excess of acetic acid, but need not be perfectly dry, is drawn through the solu-

tion, when an insoluble alumina soap is formed on the fibre, which adheres so that neither water nor mechanical means can remove it. A little undecomposed ordinary soap remains in the fabric, and it has, consequently, after drying, a soft, slippery feel, which is peculiar and not generally liked. Some persons try to prevent this by adding alum or solution of sulphate of alumina to the soap bath. This is foolish, as by so doing they destroy part of the soap without improving matters. We achieve the object rationally by passing the soaped fabric through a solution of alum or sulphate of alumina of from 1° to 1½° B. The fabric is then rinsed, which may be done in hard water, and dried. It will then have the feel of the original unsoaped article, and will be undistinguishable from it in appearance.

It is only in a very few cases that a treatment with soap solution is considered sufficient. It is nearly always customary to put indiarubber, paraffin, etc., into the fabric together with the insoluble alumina soap. This is easily done, as the soap solution has the property of forming emulsions with fused waxes and paraffin, with petroleum, or with solution of indiarubber, etc. These emulsions remain perfect for days together, and will stand frosty weather if not too severe. Instead of beeswax we use Japan or Carnauba wax. The indiarubber is dissolved in paraffin, linseed oil, with addition of palm oil.

A specially good result is got with a soap prepared as follows: Dissolve chopped-up indiarubber in twice its weight of a hot mixture of petroleum and linseed oil. Then add thrice its weight of Japan wax, and when the other ingredients are thoroughly mixed, work in a small quantity of a concentrated solution of liver of sulphur. Then stir the whole in a boiling mixture of elaine, linseed oil and resin. Finally, saponify to a neutral potash soap with caustic potash lye. The proportions should be so adjusted that the finished product contains 10 per cent. of indiarubber. The paraffin

and the indiarubber form a perfect emulsion. The soap should be superfatted with from 5 to 10 per cent. of palm oil, added to it in a state of fusion. The emulsion can only be separated by the action of acids or direct steam. It is used hot for the soaping process above described. It need hardly be said that it must not be heated by direct steam. Even this emulsion should not have alum or aluminium sulphate added to it, as those salts partially decompose it and cause marks of separated indiarubber to appear on the fabric.

As the soaping proceeds, the bath tends to get weaker and to be unable to keep the indiarubber emulsified. Hence it must be kept up to strength with hot, strong soap solution to prevent the indiarubber from separating. The soaped pieces are, as is the case with ordinary soaping, passed through a weak solution of alum or sulphate of alumina. But they are not rinsed, so that after having been kept for a few weeks they become covered with a white dust, which is removed with a brushing machine. In any case, it is advisable to put the dried pieces through the brushing machine to get rid of all mechanically adhering matter, and to give them a uniform appearance. The brushing machines usually consist of four brushing rollers close together, which can be set in rapid rotation. The goods enter it so that two of the four rollers act on each side of the piece, and send the dust into a large box placed below the machine. The fabric is generally calendered to smooth and lustre it. This is done by subjecting it to heavy pressure between the polished surfaces of steel cylinders carefully set in a strong frame and driven by belts, spur wheels or friction gearing. The motion must be perfectly smooth and steady.

The pressure used depends upon the nature of the fabric. Linen, hemp and cotton will stand stronger pressure than wool or silk. The looser the fabric is woven, too, the less the pressure must be, while strong and closely woven goods require a high pressure for their proper treatment. Care

must, however, be taken that the fibres are not crushed or flattened, as is too often done with waterproofed goods. It is a matter of opinion whether the rollers of the calender should be all steel or steel and paper in pairs. The writer is on the side of all steel calenders, which, he thinks, impart a better lustre by their stronger action. The calenders used

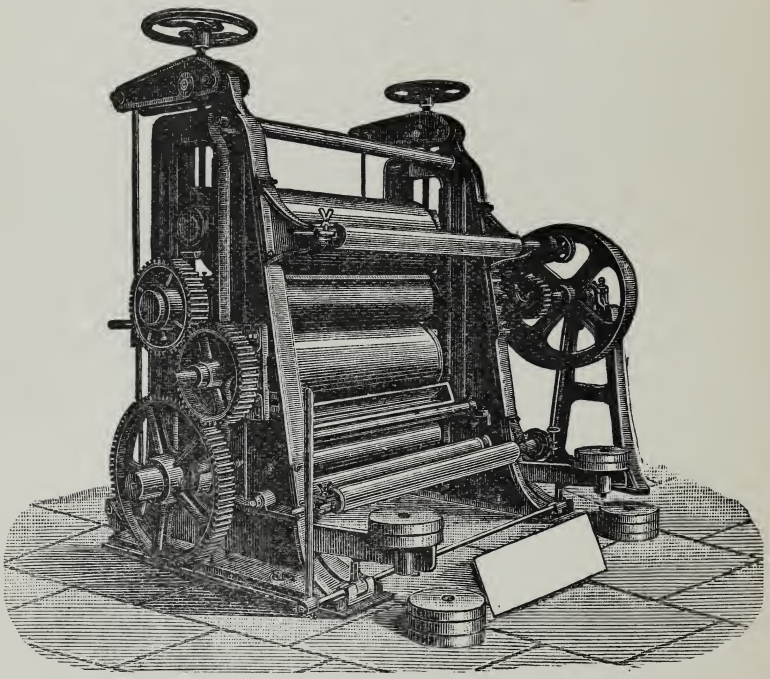


Fig. 20.

are generally of the friction or "universal" type. Fig. 20 shows one with four to five rollers. Two are usually of paper. One of the rollers can be heated, either the uppermost or the middle one. The pressure is effected by levers with double spur-gearing. The friction arrangement can be thrown out of gear, so that the apparatus can be used as an

ordinary calender. To ensure that the goods shall come clean from the calender, the greatest care must be taken to keep the cylinders clean, and this cannot be done if the goods have been badly waterproofed. They must be free from excess of soap, or the rollers will be perpetually dirtied with soap.

The finished goods are first tested as regards appearance. The eye must be incapable of distinguishing them from the unwaterproofed fabric. Samples are tested by making bags of them, which are filled with water. The outside of the bag must remain dry; if the wet shows through the fabric has been badly waterproofed or did not leave the calender thoroughly dry. In the latter case a fresh drying merely is required. In the former case, as neither basic acetate of alumina nor alumina soap is removable by water, the fabrics must be freed from those bodies with dilute hydrochloric or, preferably, acetic acid, rinsed, washed with soap and soda and waterproofed all over again. The fabric has by this time, however, become sensibly tendered, so that the new waterproofing best takes the form of a painting over with tar or with solution of indiarubber.

We may finally mention that waterproofed goods are often further treated with paraffin by methods to be described later. There is no object in paraffining a well-waterproofed fabric, as the waterproofness is not thereby increased. When the fibres have been filled up with basic acetate of alumina, or the corresponding alumina soap, no room is left in them for paraffin or ceresine, which can only be plastered over the outside of the piece, which causes the fabric to acquire a greasy and very unpleasant feel. Spoiled goods can, however, be renovated with paraffin, but the waterproofness thus acquired is not very satisfactory and does not last very long.

## CHAPTER VI.

### WATERPROOFING WITH PARAFFIN.

A WATERPROOFING method which is greatly in vogue consists in the use of solutions of paraffin, ceresine, wax, and the like, in benzole or petroleum benzine. The solution fills the cells of the fabric and envelops them, and the solid matter is left behind when the solvent evaporates. Both the solid material used and the solvent must be free from smell, or an odour will cling persistently to the finished goods.

By paraffin we understand solid hydrocarbons. Ozokerite is a natural form of it, and it can be got by the dry distillation of brown coal, turf, etc., and suitable treatment of the distillate of paraffin oils. Ozokerite occurs largely in Galicia, Hungary, the south of Russia and in America, in pieces waxy-yellow or black in colour. It is purified by repeated treatment with sulphuric acid, and bleached with animal charcoal, after it has been purified from volatile matter by distillation with superheated steam. The purified product is called ceresine. It is minutely crystalline, odourless, fuses at 74° to 80° C., and dissolves easily to a clear solution in benzole, petroleum benzine, ether, bisulphide of carbon, fatty oils, etc. As it is unacted on under ordinary temperatures by caustic alkalies or by sulphuric or nitric acid, it protects fabrics from injury by those substances.

Paraffin is known in commerce as hard or soft paraffin, according to its fusion point. The former fuses at 52° to 56° C., the latter at 44° to 48°. They have the same solubility and resistance to acids and alkalies as ceresine. As they are

got by crystallisation from the above-mentioned paraffin oils, it might be supposed that those oils, which also dissolve in all proportions of petroleum benzine, bisulphide of carbon, etc., would be suitable for waterproofing. Their use for that purpose, however, has several disadvantages. No properly solid mass is left behind by the evaporation of the solvent, and no crystallisation takes place. The solution, in fact, behaves like a non-drying oil. The best form to use for waterproofing is the white ceresine, which, on account of its high fusion point, resists the action of heat to which the fabric may be exposed. Such goods must, however, not come into contact with hot water, and must not be washed. Every time this happens some of the ceresine is lost, so that the material soon becomes permeable to water.

The fabrics to be paraffined must be clean so as to absorb properly, and the impregnation would be best done in a vacuum as above described were it not for the circumstance that on cooling we get a thick coat of ceresine or paraffin which is difficult to remove. In choosing apparatus for impregnation with paraffin or ceresine care must always be taken that means are provided for recovering as much as possible of the solvent, not merely on the ground of economy, as the recovered liquid can be used over again, but because the vapours are dangerous. That of petroleum benzine, for example, in hot weather or in heated rooms, may catch fire spontaneously. The apparatus must therefore be enclosed, and means provided for condensing the vapours. A very simple apparatus for the purpose is shown in Fig. 21. A is a vessel 1 metre long, and wide enough for the fabric to pass through it at full width. B is an iron vessel, the base of which stands on a plate which can be heated by steam. B has a roof-like cover, *e*. Over the ridge of this roof runs a gutter, K, from which cold water constantly flows over both slopes of the roof. The roof itself is either of corrugated iron or is covered with linen to prevent the water from running

off it too quickly. The water collects in the gutters, *i*, and the benzine is condensed inside in the gutters, *h*, whence it runs into receptacles. The working of the apparatus is as follows: The ceresine or paraffin solution is put into the box, *d*, which is then closed with a lid. The lid communicates by a pipe with the cover of the vessel, B, into which the vapours from *d* pass. The roller, *a*, provided with a brake, has the fabric to be impregnated, *b*, wrapped on it. From *a* it passes over the guiding rollers, *c*, $c_1$, $c_2$, through the solution in the box to two scrapers which remove the superfluous solution. It then enters B, where it passes over the hot plate, *f*, which evaporates the solvent. The fabric then passes out, to be rolled on the roller, *g*, over the guiding roller, $c_3$.

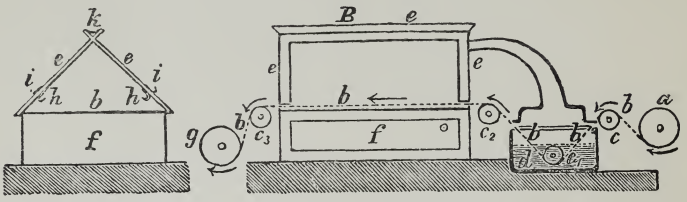



Fig. 21.

Both A and B must be tightly closed to minimise the escape of benzine, and the temperature must not exceed 50° to 60° C., so that the ceresine is deposited, but not fused. In winding the impregnated fabric on to *g*, the workman must proceed slowly, so that the impregnation may be thorough, and that the fabric may leave B dry. This apparatus can be varied in many ways, *e.g.*, by blowing in hot air under the fabric in B with a fan instead of using the hot plate. The hot air has then to pass into a condenser to condense the benzine vapour from it. Whatever care may be taken the drying is not perfect, and a supplementary drying is required. This is best done in open sheds, so that the open air enters from all sides.

Another method of impregnation is to pour fused ceresine over the fabric instead of using a solvent. This is done by rubbing the fabric over a block of ceresine, and then passing it over hot cylinders to melt into it the ceresine it has rubbed off. This method, however, gives uneven results, some places being left imperfectly waterproofed while others receive more ceresine than is needed. Again, the powerful friction caused by the pressure makes the material sticky. Thin fabrics will not stand the process at all, as they tear under it. All attempts to make the method a success have failed. It has been found impossible, even by means of rollers, to apply the small quantities which must not be exceeded for most fabrics. Dipping into the molten ceresine gives even worse results, for the fabric becomes so over-saturated as to be quite stiff.

The following is a process free from these drawbacks: The hydrocarbons, ceresine, paraffin, or mixtures of them and similar bodies, are not applied either in solution or in a solid or viscid form, but in a melting state by means of a special apparatus, which not only makes it possible to regulate exactly the amount of waterproofing material taken up by the fabric, but to distribute it with absolute uniformity. This is managed by rotating a metallic roller in contact with the solid hydrocarbon, so that it gradually carries away portions of it and puts them on to the fabric, which passes between the roller and a trough. This trough is heated, and fuses the hydrocarbons on the roller where they come into contact with the fabric, so that they are soaked up by the latter as fast as they are fused. There is neither pressure nor friction that can be injurious to the fabric, as the rollers travel at the same rate as the fabric, the smooth inside of the hot trough acting as a flat iron.

An apparatus intended for use in this process is shown in Fig. 22. It consists of the impregnating substance, *a*, and its container, *a'*. The impregnating substance of paraffin, ceresine or wax, with or without admixture of indiarubber or

guttapercha, is moulded so as to fit as much of the surface of the roller as is intended to come into contact with it. This block is somewhat tapered below, and fits into the open container, $a'$, which contains springs to press the block against the roller. B is the metal roller for removing waterproofing

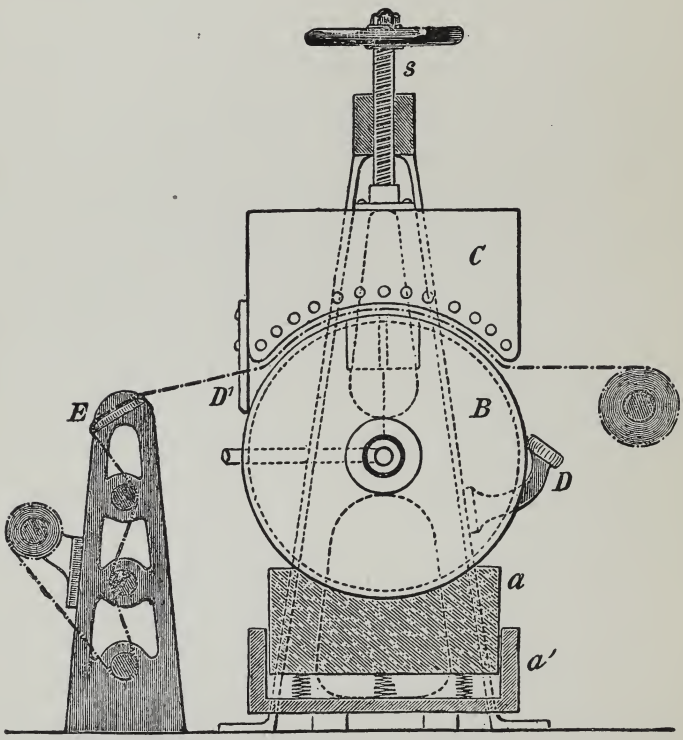



Fig. 22.

material from the block, and its surface may be rough or polished. The interior of the roller is kept sprayed with water, through a hollow axle, so as to keep the temperature of the roller, which is of the greatest importance in getting a uniform abrasion of the hydrocarbon block, at the proper

point. The flow of water is regulated automatically by a thermostat. We thus obtain security against any fusion of the hydrocarbon by the roller, and prevent the temperature of the latter from falling too low The trough, C, fits accurately to the upper part of the roller by its smooth concave surface of steel, bronze or copper. The amount of the roller covered by the trough is determined by the amount of heat required to fuse the hydrocarbons.

The interior of the trough is heated by gas, steam, or in any other way that may be desired, and rests on the roller, against which it is pressed by levers or by the screw, *s*. The scraper, D, is intended to remove fluff and loose threads which might hang from the lower side of the fabric on to the roller, and the scraper, D′, removes any excess of waterproofing material. D consists of a metal or wooden bar, with the edge in contact with the roller, covered with india-rubber or cloth. The hydrocarbon block is usually made a little wider than the fabric to be waterproofed, so that parts of the roller which do not touch the fabric become coated with it. To prevent this excess of hydrocarbon from getting under the trough without being absorbed by the fabric, an adjustable scraper, D′, is put on both sides of the trough and removes the excess. E is the roller from which the fabric passes to the machine, and E′ that on which it is rolled after going there.

Waterproofed fabrics made by this method are decidedly different from those made with hydrocarbons in solution. The waterproofing substance lies more externally and does not penetrate into the cells, as it does in impregnation with solution.

The goods are finally calendered, and for this class of goods the lever pressure calender shown in Fig. 23 is very suitable, as it has a large capacity, causes no stains, and goes very steadily with very little power or attention. It is driven by friction gear, sometimes with two pulleys of

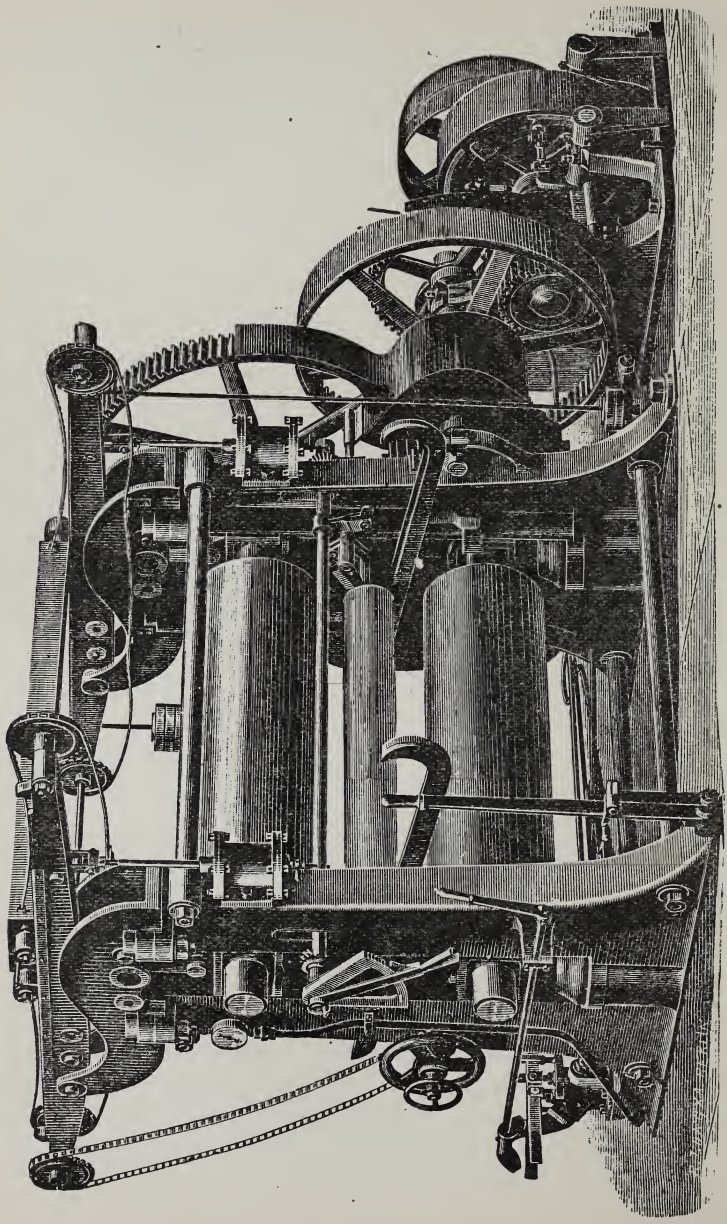


Fig. 23.

different diameter for slow and rapid working, so that the machine minder can put the work through with exactitude, and sometimes of the same diameter for reversing, with open and cross belts, so as to drive the calender one way or the other according as the fabric is put into it.

It has already been stated that other substances can be mixed with ceresine of paraffin, provided that they will dissolve with them in benzine or carbon bisulphide. A very good example of a composition recommended for waterproofing hempen fabrics is given in the following recipe :—

| | |
|---|---|
| Soft paraffin . . . . | 240 lb. |
| Beeswax . . . . | 8 ,, |
| Ceresine . . . . | 8 ,, |
| Poppy oil . . . . | 2 ,, |
| Dissolved in benzine . . | 1600 ,, |

The soft paraffin being greatly in excess of all the other solid ingredients, its fusion point is not very perceptibly raised, and the minor constituents do not exert much effect on the waterproofing, so that the result is not better but worse than if hard paraffin or ceresine had been used alone.

## CHAPTER VII.

### WATERPROOFING WITH AMMONIUM CUPRATE.

Many people prefer waterproofing with ammonium cuprate, a process first brought into use by Hime, to every other method. In the opinion of the writer there is no difference between this method and that consisting in the use of acetate of alumina. Regard must also be paid to the way in which the waterproofing is done. If we use solution of cuprate of ammonia, in which remnants of silk, cotton or parchment have been dissolved, a superficial combination of the solution with the fabric takes place, the surface of the fabric becomes gelatinised, and all the pores are filled up as if they had been covered with an oil colour. If, on the other hand, we follow the treatment with ammonium cuprate with one with ammonium sulphate and aluminium acetate, the copper dissolves as sulphate and nothing remains in the fibre but basic acetate of alumina, as the acetic acid is evaporated by the drying. The copper can, of course, be recovered from the liquors.

Vegetable fibre, especially linen and hemp, rapidly absorbs an ammoniacal solution of cupric oxide, and partially dissolves in it. This, however, does not make the fabric waterproof, even if cupric oxide is precipitated on the fibre by subsequent treatment with caustic potash. This precipitation of metallic oxide can be done from an ammoniacal solution of oxide of zinc, cobalt or chromium, without using a caustic alkali. This is constantly done by dyers in mordanting. If it has been decided to use ammonium cuprate,

the first essential is to prepare that reagent correctly. A process often employed is to boil copper turnings with solution of carbonate of soda, rinse them with water, and then expose them to the air in contact with ammonia of sp. gr. 0·91, which contains 25 per cent. of $NH_3$ or 227 grammes to the litre. This is an unpleasant process, and must not be done in rooms where people are working. The solvent power of the ammonia is increased by the presence of a little sal-ammoniac. A more rational method is to oxidise the copper in a rotating copper cylinder provided with a stirrer.

The simplest and quickest method, however, is as follows: A cold solution of sulphate of copper is precipitated with the exact amount of caustic soda necessary, or slightly less. The temperature must be below 20° C. or the precipitate will be black instead of blue, and the leaving of a small excess of copper sulphate is an additional precaution against this. The precipitate is washed with condensed water till the washings give no precipitate, or next to none, with chloride of barium. The precipitate is then pressed to get rid of most of the water, and dissolved in just enough ammonia of sp. gr. 0·93. The strength of the solution in copper is then determined, and enough additional ammonia is added to make the solution contain 18 to 20 grammes of copper to the litre. This solution must not be confounded with that obtained by precipitating sulphate of copper solution with caustic ammonia, and then adding an excess of the reagent so as to re-dissolve the precipitate. In this way we get a double salt of ammonium and copper which cannot dissolve vegetable fibre. Cuprate of ammonia, on the other hand, dissolves incredible quantities, and also dissolves silk.

The fabric to be waterproofed is drawn through the copper solution at a carefully regulated speed, so that the fibre is partially parchmentised, and so that the cellulose in solution has time to deposit in and between the threads. Scrapers remove the excess of solution, and pressure rollers consolidate

the remaining mass, while the ammonia is rapidly volatilised by heat or by a current of air. The apparatus must therefore be one which will not permit the ammonia vapour to reach the workpeople. The vapour is drawn off and absorbed by dilute sulphuric or acetic acid. The goods must be finally calendered. This method is generally confined to dyed fabrics, as it imparts an undesirable appearance to white goods. Such fabrics are freed from copper as above described, or a soluble chromate or bichromate is added to the solution of ammonium cuprate. This makes the colour of the finished fabric better and paler. These oxides are put into the copper cylinder with the copper turnings, and a corresponding amount of them goes into solution. The colour caused by oxide of copper can also be altered by treating the impregnated fabric with a solution of a sulphocyanide or a sulphurous acid, or with sulphuretted hydrogen.

Ignaz Breitenfeld first soaks the fabric with egg albumen, then with a cyanogen compound or tannin, and then ammonium cuprate. The goods are then sharply dried. The tannin may be used first and the albumen next. The copper oxide forms with the other substances coloured precipitates, so that we get waterproofed fabrics of various colours, which, nevertheless, have no beauty or lustre. Other reducing agents, such as acid solutions of ferrous sulphate or stannous chloride, can also be used. We have already mentioned that ammoniacal salts of other metals can be substituted for the ammonium cuprate.

Hime precipitates the copper from a solution of ammonium cuprate saturated with cellulose, by putting into it strips of zinc, and hence obtains a colourless solution of cellulose in ammonium zincate. Into this thick liquid he dips his fabrics, so that they are entirely soaked with it. He then wrings out the excess of solution and dries the goods on a calender. Felton uses combinations of the chloride or sulphate of cadmium of zinc with ammonia. He makes his solution,

for example, with 3 lb. of crystallised zinc sulphate, or the same weight of zinc chloride solution of sp. gr. 1·44 (60 per cent.) and 2 lb. of ammonia of sp. gr. 0·872 (34 per cent.). The fabric is led over guiding rollers into a chest lined with lead, at the rate of 25 to 35 metres a minute, according to the thickness of the fabric. Here it passes through the solution and becomes thoroughly soaked. On leaving the bath the fabric passes through wringing rollers, which consolidate it to some extent as well as remove the excess of liquid. It passes next to the drying room where it is exposed to a temperature of 43° C. till quite dry.

Fabrics waterproofed with ammonium cuprate have a somewhat harsher feel than those done by the more usual methods, but possess, on the other hand, more lustre, especially if remnants of silk have been dissolved in the ammonium cuprate. Inspection shows that the pores of the fabric are covered with a thin skin of cellulose. The fabrics are air-tight as well as water-tight, so that these are useless in cases in which permeability to air is a desideratum.

## CHAPTER VIII.

### WATERPROOFING WITH METALLIC OXIDES.

Other metals in the form of insoluble soaps behave like copper. The salts used for impregnating fabrics with these soaps are, besides those of iron already mentioned, those of aluminium, antimony, tin, lead and zinc. These metals give salts soluble in water, in some of which the acid radicle contains the metal, while in others it is in the basic radicle, all of which on decomposition give insoluble hydrated oxides.

If we mix a solution of potassium aluminate with one of zinc acetate, we get a precipitate consisting of the hydrated oxides of zinc and aluminium, and this precipitate can evidently be formed upon a fabric. These oxides, however, are not sufficiently water repellent, so that absolute waterproofness is not certain, and it is best to have recourse to the metallic soaps. These soaps have all sorts of colours, so that not all of them can be used. Besides, some of them are too expensive for ordinary use, as cheapness of production is a fundamental condition of the successful manufacture of waterproofs.

When it is a question of waterproofing a brown material, iron soap can be used. We first soak the fabric in solution of acetate of iron and then in a solution of soap. It is better, however, to dye the fabric and waterproof it with aluminium acetate.

## CHAPTER IX.

### COLOURED WATERPROOF FABRICS.

Although dyeing is a special branch of chemical technology, and is carried out in special factories, the waterproofer cannot do without dyeing, as his products are often required to be black, brown, green, yellow, and other colours. We shall not here describe the theory of dyeing, but refer the reader wanting information on it to special works. We will only mention that every material is not able to take up every dye, and that the most varied differences exist in this respect. Wool, cotton and silk, for example, behave differently from hemp, linen and jute to certain dyes. In dyeing, therefore, the nature of the dye and the nature of the fabric have both to be considered.

Some dyes dye directly; others, however, require fixing by means of a mordant. The mordant forms a triple combination with the fabric on the one hand and with the dye on the other. According as they require or do not require a mordant, we classify dyes as adjective and substantive. As mordants, metallic salts are the substances most commonly used, and especially those of antimony, aluminium, chromium, fluorine, tin, copper and iron. Organic bodies, such as tannin, are also used to deposit insoluble compounds, called lakes, in the fibre.

For dyeing, the natural dyes, logwood, fustic, etc., are still largely used, and by some persons exclusively, but there are many artificial dyes which answer every purpose perfectly. The dyeing of fabrics of hemp, linen and jute, which are

those chiefly used in waterproofing, is done, with a few exceptions, like that of cotton, with the sole difference that the temperature used must be higher and must be maintained for a longer time. The artificial substantive dyes go better and more uniformly on to the fibre than the natural dyes, and penetrate better, especially when baths are, as is shown to be advisable by experience, somewhat concentrated.

Hemp, linen and jute are naturally of a darker colour than cotton, and this is taken advantage of in dyeing dark shades, as it saves time and dye and gives a fuller shade. Such fabrics must, on the other hand, be bleached before dyeing them light colours. Whether half or whole bleached material is used, it is always necessary to scour it before dyeing by boiling it with a 10 per cent. solution of crystal soda or an equivalent solution of ammonia or waterglass. The fabric is then centrifuged full width, boiled for two hours in plain water to rinse it, and then dried nearly completely. By this treatment the receptivity of the fibres for mordant and dye is increased, and the dye also goes on more evenly.

Whether the one-bath or two-bath method should be adopted depends on circumstances and on what is expected from the finished articles. Many dyes dyed in a single bath (especially black) rub off when the same dyes dyed by the two-bath process do not. As a rule, natural dyes give much faster colours in a single bath than the adjective coal-tar colours. The latter generally rub, even if they have been after-coppered.

The dyeing process is done with the same apparatus as is used in impregnating, that is to say, jiggers or padding machines. The same apparatus is used for mordanting. To give recipes for the various dyeing processes would be useless. Experience will soon show how to produce the desired shade. Moreover, new artifical dyes, both adjective and substantive, are discovered almost daily, and the dye manufacturer supplies the fullest information as to the way in which all his

dyes are to be used. As each factory has its own methods of preparing artificial dyes, so that they acquire a characteristic shade, the waterproofer must choose a manufacturing firm once and for all, and then always buy his dyes of the same if he wants to secure uniformity of appearance in his own products. It is best to use substantive dyes for the fabrics in question. For black either an iron, an aniline or an alizarine black can be used. Properly employed they do not rub. After dyeing dry thoroughly and calender. The dyeing does not always waterproof the stuff, so that it must be waterproofed afterwards. It is therefore necessary to select dyes which will not suffer from subsequent treatment with acetate of alumina and soap or with cuprate of ammonia.

The dried dyed goods may be waterproofed by treatment with a solution of acetate of alumina of 5° B., as above described, then drying, finally passing through a 2 per cent. solution of soap. A still better method is to treat them for some hours with a 2 per cent. solution of sulphate of copper and then with the 2 per cent. soap solution. For the sulphate of copper we may substitute other copper salts, or salts of nickel, zinc or tin. This treatment increases the fastness of the dye to light, although the metallic oxide does not enter into the composition of the lake but only lies on the fibre in a thin layer, thick enough, however, to absorb a part or perhaps all of the actinic rays which would otherwise reach the dye.

The dyed waterproofed goods must be tested for fastness :—

1. To light and air.
2. To washing.
3. To wear.
4. To perspiration.

No one has as yet succeeded in making dyes altogether fast to light and air. Every dye exposed to their influence changes sooner or later, turning pale or to a different shade. We know by experience that certain dyes vary in fastness to

light and air, especially according to the method of the dyeing. In considering new dyes and new dyeing processes, recourse should always be had to the light test. The simplest and surest but not the quickest way of doing this is to wrap half the dyed sample of cloth in a close sheath of paper, which can be gradually drawn off. The date of the beginning of the experiment is marked on the paper, and the half-covered piece of cloth is exposed to light. At intervals the proper sheet is partly withdrawn, so that the amount of cloth exposed to the light is increased daily or at longer intervals. The effect of the light on the dye in various periods of time is thus easily seen. No change should appear with good dyes before the lapse of twenty to thirty days in summer and about fifty days in winter. Special apparatus can be obtained to arrive at the result in less time.

Fastness to washing is hardly worth mentioning, as very few dyes show absolute fastness in this respect. Nevertheless, they must be very resistant to the free alkali found in many soaps, especially soft soap, and not bleed when treated with them. Many coal-tar dyes do so, however, more or less. Natural and mineral dyes never bleed. The test for fastness to washing is carried out by rubbing the dyed fabric with a piece of white cotton cloth for two or three minutes in a $\frac{1}{2}$ per cent. soap solution at 40° C. The two pieces are then left lying in the soapy water for twenty minutes. They are then rinsed, left another twenty minutes in the rinse water, wrung and dried. In most cases the white cotton will be found partially dyed. The temperature of 40° C. must not be exceeded for a fair test. Many dyes which will not bleed at 40° C. do so at 60° to 70°.

Fastness to rubbing in wear is very necessary for dyes for waterproofs, such as tent cloths, waggon covers, etc., which get rubbed by constant folding and unfolding. There are so many dyes on the market which are fast to rubbing that it is unnecessary to use others. The test is carried out by

rubbing the coloured fabric by the hand on white unstarched cotton or on not too smooth white paper.

Waterproof fabrics which have to come into contact with the human skin have to be tested for fastness to perspiration. This is done by making a $\frac{2}{5}$ per cent. solution of acetic acid, heating it to the temperature of the human body (37° C.), and then rubbing the dyed sample in it forcibly for a few minutes. The sample is then dried at the ordinary temperature of the room, and without rinsing, between two sheets of parchment paper. The effect produced by several repetitions of this treatment not only tests the fastness to perspiration, but also whether the waterproofing has been well done. Fabrics waterproofed on one side with indiarubber are usually tested for fastness to acid by soaking them for several hours in dilute sulphuric acid, drying, and observing the effect.

## CHAPTER X.

### WATERPROOFING WITH GELATINE, TANNIN, CASEINATE OF LIME, AND OTHER BODIES.

We here mention certain processes which are rarely used, and which differ essentially from those already described, as they depend upon the formation in and upon the fibre of substances which repel water mechanically, or are simply substances which fill up the interstices. Thus we have two classes of process. In the first class we have waterproofing with gelatine, glue, tannin, caseinate of lime and the like; and in the second, waterproofing with tar, tar oils and similar bodies.

Waterproofing goods with glue and tannin is based on the fact that by the action of tannin or bichromate compounds insoluble in water are formed. In this sort of manufacture a proper choice of the fabric plays a very great part, and it should only be applied to fine and closely woven cloth, in which the threads are not twisted together. Each thread must be fairly free or the solutions cannot penetrate it properly. It is of first importance for the success of the process that both solutions (tannin and glue) should penetrate fully. In this connection it must be remembered that contact with the water of the solutions makes the fabric closer by swelling up the threads.

If the fabric is dipped directly into strong solutions of glue and then of tannin, the glue will only become insoluble on the outside, and that which had penetrated deeper into the fibre will be unchanged, having been protected by the

superficial insoluble layer. If a section of such a defective fabric is examined microscopically, we see at once by the paler colour of the interior of the thread that the tannin has not penetrated thoroughly. Hence we begin by treatment with a very weak solution of glue, prepared by leaving glue broken small in a hundred times its weight of water for twenty-four hours. By that time the glue will have swelled up, and the whole is boiled up, with continuous stirring, so as to get a perfectly clear solution, in which the fabric is boiled for ten to fifteen minutes. This time is no more than is necessary for complete penetration. The fabric is then well wrung between two rollers placed right over the glue bath, so that the excess of glue solution runs back into it. The fabric is then hung up, and when nearly dry is passed through a solution of tannin. This solution may be made from tannin itself or from a tannin extract, or by boiling galls or oak bark in water. The tannin solution can be used fairly strong, as only so much of it is taken up as corresponds to the glue present, and it can be used over again as long as it can supply the tannin required, and can then be reinforced with more tannin as required.

It is not necessary for the fabric to stay long in the tannin, as it reacts very quickly with the glue. The tannined fabric is again hung up to dry, and when quite dry is washed in plain water to remove any excess of tannin. The whole process from the beginning is then twice repeated. After this second repetition there is so thick a layer of tannate of gelatine on the fabric that the dry cloth has acquired considerable solidity and a smoothness which recalls that of leather. We then pass to stronger glue solution, using three or even four parts of glue per hundred of water, but never exceeding the latter limit. After the glue bath the fabric goes through the tannin bath, and we finally get the fabric fairly thickly coated with tannate of gelatine. By repeatedly treating with glue and tannin alternately this coating can be made

as thick as desired, and we finally get masses in which the texture of the fabric is entirely hidden, and especially if the fabric has been calendered under heavy pressure after waterproofing.

The colour acquired by goods waterproofed in this fashion is a more or less dark leather brown. The hue depends chiefly upon that of the glue, some sorts of which are much darker than others. The waterproofed fabric will take a fine black. It is first painted over with a decoction of logwood, and then, after drying, gone over with a sponge with a very weak solution of bichromate. Ferrous sulphate may be substituted for the bichromate, but the result is not so good. Other colours may be got by mordanting as above, but with alum, and giving as the second coat after drying a decoction of Persian berries, redwood, etc. By means of anilines we can get any colour without preliminary treatment. It must, however, be remembered that, if the fabric is to be dyed a light shade, only the palest glue must be used for the waterproofing. Dark glue will spoil the effect of the dye. Goods waterproofed with glue and tannin are of very subordinate importance. Exposure to wet rapidly destroys them and makes them lose their strength.

Muratori and Landry treat the fabric with a solution made in three separate operations :—

1. One hundred lb. of potash alum are dissolved in 10 gals. of boiling water.

2. In another vessel 100 lb. of glue are soaked in cold water till the glue has trebled its weight. The remaining water is poured away, and the vessel is heated to liquefy the glue. When the glue is boiling, 5 lb. of tannin and 2 lb. of soda waterglass are put into it.

3. The two solutions are boiled together with constant stirring.

When the mixture is complete it is allowed to cool to a jelly. To waterproof the goods some of this jelly is boiled

with water (1 gal. to 1 lb., or a little over) for three hours, adding water to compensate for the evaporation, so as to keep the volume of the solution constant, as shown by tests of its specific gravity with a hydrometer. The bath is then allowed to cool to 80° C., and the fabric is soaked in it for half an hour and then stretched out horizontally for six hours to drain. The fabric must be kept horizontal, so that the solution remains uniformly distributed through it. The drainings are collected for using over again. The fabric is then dried in the open air, or in a drying room, still in the horizontal position. If a drying room is used the temperature of it must not exceed 50° C.

It is said that this method gives heavy and very wet-resisting goods, which in no way hinder evaporation from the body. The final calendering is done between rollers heated to 50° C. If the goods are waterproofed by Muratori and Landry's method after being dyed, the treatment fixes the colour, so that the dyeing should be done first, remembering, nevertheless, that in light shades only alum free from iron and the very palest glue may be used.

Muzmann and Krakowitzer dissolve 10 lb. of gelatine and 10 lb. of tallow soap in 30 gals. of boiling water, and mix the solution in 4 gals. of water in which 15 lb. of alum have been dissolved. The whole is boiled for half an hour, and then allowed to cool to 40° C. At that temperature the fabric is thoroughly soaked in it, dried, rinsed, again dried, and finally calendered. In this process the alum partially decomposes the soap, forming either free fatty acid or an acid alumina soap. The gelatine forms an insoluble compound with the alum. The free fatty acid or acid soap is mostly carried down on to the fibre by the precipitate formed by the alum and the gelatine.

A. Dumas soaks the fabrics first in a 7 per cent. solution of gelatine at 40° C. After a few minutes the goods are wrung between rollers, dried in the air, soaked for a few minutes in

a 3 to 4 per cent. solution of alum and then thoroughly dried. In another process the fabrics are thoroughly soaked in a solution of 8 lb. of alum, 4 lb. of isinglass and 2 lb. of white soap in 20 gals. of water. They are then passed through a second bath of 8 lb. of sugar of lead dissolved in 20 gals. of water, and finally dried.

A curious method of waterproofing has been proposed, which consists in passing the fabric repeatedly through a solution of alumina soap in oil of turpentine. A fabric treated like this will retain the smell of the turpentine for years.

Sandtner dissolves resin soap completely in hot water, and precipitates it with chloride of calcium. The precipitate is at once washed, dried and ground to a fine powder. Seventy lb. of the powder are then mixed with 30 lb. of a uniform mixture of resin, linseed oil and oil of turpentine. The paste so formed is worked into the fabric with a brush.

Schulke dissolves 580 lb. of gelatine by boiling in a mixture of 750 lb. of glycerine with 150 gals. of water, and then adds a solution of 40 lb. of bichromate of potash and a solution of $\frac{1}{2}$ lb. of salicylic acid in spirit. The finished solution must be kept in the dark. The fabric is thoroughly soaked in it, and then exposed to the light till the original green colour of the soaked fabric has quite disappeared.

A mixture recommended for waterproofing woollens and half-woollens consists of 100 lb. of glue and 100 lb. of alum, dissolved in an amount of water varying with the weight of the goods and the hardness of the finish desired. The mass is then mixed with 5 lb. of tannin, 2 lb. of waterglass and 10 gals. of water, and the fabric is soaked in the final mixture at 40° to 60° C. Thick sacking or waggon-cloths are first impregnated with waterglass, then with a solution of alum, or sulphate, or acetate of alumina. They pass then through a weak superfatted soap bath, and are finally slightly calendered.

The caseinate of lime method was first described by Chevellot, and is said to ensure the fabric retaining its softness and perviousness to air and to enable it to be washed with soap, benzine, etc., without interfering with its waterproofness. The process is conducted as follows: Casein precipitated from milk is mixed with about five times its weight of water, and the whole is well stirred to a creamy liquid. This is gradually mixed with a weight of slaked lime equal to about $\frac{1}{40}$ of that of the casein. At the same time half the weight of the casein in soap is dissolved in twelve times its weight of water, and the soap solution is mixed with the other. The fabric is impregnated with the mixture till its weight is doubled. The fabric is next dipped in a solution of acetate of alumina, which makes the caseinate of lime insoluble and forms a margarate of alumina with the alkaline soap. The fabric is then passed quickly through the oily boiling water, and finally dried and calendered.

The pure casein required for the preparation of the caseinate of lime is got by letting milk stand in a cool place, and carefully removing the whole of the cream, skimming until no more cream rises. The milk, perfectly free from cream, is coagulated by adding lactic acid until that reagent gives no further precipitate. The precipitate of casein is washed and dried. The milk also may be left to get sour and throw down the casein spontaneously. When the milk has been precipitated, the casein is washed absolutely free from acid with distilled water. The casein is then boiled, wrapped in a cloth, in water, to get rid of the last traces of fat. It is then dried in a warm place on blotting-paper, when it shrinks into horny masses. If quite dry, it will keep perfectly for a long time. To dissolve it for use, it is first soaked in water.

Benzinger's collodion process must be mentioned. He dissolves 10 lb. of pyroxyline in about 2 lb. of spirit mixed with acetic acid, acetic ether, acetone, or other solvent of nitrocellulose. About 3 lb. of castor oil is also added to

give the necessary suppleness. The fabrics are soaked in the finished mixture, and this must be done in a very hot room. The fabric remains in the bath for two to three minutes. It is then hung up to drain, and the pores become filled with the solution. When dried, the fabric is too hard for use, and to give it the necessary suppleness it is laid upon heated polished metal plates and subjected to a very high pressure. This treatment drives the oil with which the plates have been previously smeared into the pores of the fabric, thereby completely suppling it. The same result can be got by calendering between the oiled rollers. The waterproofing solution may be made from celluloid scraps, but the result is neither so clear nor so lubricating as that made from pyroxyline. The inventor says that the process is very inexpensive (which may be doubted) and that the fabrics treated thus are more durable than those waterproofed with indiarubber.

## CHAPTER XI.

### MANUFACTURE OF TARPAULIN.

Tarred fabrics as waterproof goods are remarkable for cheapness and durability, and are hence largely used for making waggon cloths for covering over goods which have to be protected from the rain. Tarpaulin, if properly made, is only coated on one side, and the coat should be smooth and uniform, should not rub off, should have no disagreeable smell, and should not become sticky in the sun.

Ordinary gas tar as it comes from the gas works must not be used until it has been freed from its more volatile parts by boiling. Tar-boiling is an operation which must be conducted with certain precautions, not only on account of the danger of fire resulting from the inflammability of the escaping vapours, but on account of the disagreeable smell produced. On a large scale stills are used, but on a small scale the tar is merely boiled in an open shed over a naked fire. It is unnecessary to describe the process in detail, but the tar must not be heated to more than 300° C., and this temperature is quite sufficient to volatilise the oils which make the raw tar unfit for waterproofing. The fabrics to be tarred are stretched on frames if in small pieces and wound on rollers if in large. In the latter case there must be an arrangement for maintaining the tension while the cloth is off the feed roller and being coated.

Such an arrangement is shown in Fig. 24. The fabric is wound lightly on the feed roller. Strings are attached to the end which leaves the roller last, so it can then be fastened

to another place. The other end of the piece has also strings attached to it. These must have the same length as the piece, and are stronger than those attached to the other end. They are fixed to the roller, W, which is at such a distance from the roller on which the fabric is first wound that the fabric can pass from one roller to the other. To prevent sagging, which would be sure to occur with long fabrics, the cloth goes first over the spreading table and then over strong stretched strings or a netting. The roller, W, on to which the fabric is wound has a brake, and the roller, W*i*, on which

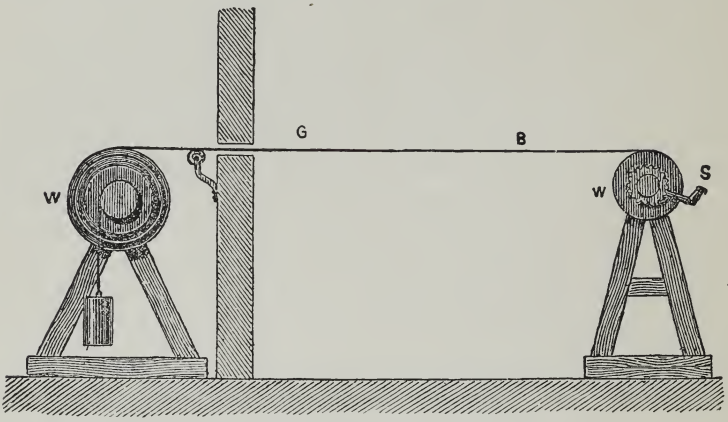



Fig. 24.

the strings are wrapped has a pawl and ratchet wheel, so as to deliver the fabric always under tension. The feed roller is put as near to the wall as possible, in front of the spreading table, and passes through a slit in the wall. The spreading room must be kept hot (25° to 35° C.) so that the fabric may dry rapidly.

Two methods of spreading have to be considered, hand spreading on frames and mechanical spreading. The former is only practised in small pieces of fabric. It is done by having an iron pan full of hot tar so hung over the fabric to

be coated as to be readily accessible and to be capable of being moved from place to place. This is best done by stretching a strong horizontal wire above the fabric. This wire carries a pulley and a hook on which the handle of the pot is hung. The tar is then applied, by means of flat brushes with strong short bristles, by two men who stand facing each other and do half the fabric each. The work must be done while the tar is hot, or else it will not spread. A third man is consequently employed to replace the pot, as soon as it is too cool, by another fresh from the fire. The part of the fabric being operated upon rests upon a heated table of metal, or contact with the fabric would chill the tar so that it would be almost impossible to spread it uniformly. Each painter holds a brush in one hand, with which he spreads the tar, and in the other a flat ruler, with which he goes forcibly over the coated parts to equalise the thickness of the tar coat. The kettles are replaced with fresh hot ones as they get cold or emptied. As the fabric is coated it is wound up, so that the workmen need not leave their places as they apply the tar. If a heated spreading table is not wanted, the fabric is passed over a table of planed wood about 20 inches long and of the same width as the fabric.

Spreading machines of various designs are intended to secure that the tar shall be of uniform thickness all over the fabric. They consist of two principal parts, a spreader and a stretching apparatus. Fig. 25 shows one of the machines. The fabric rolled on the roller, W, goes between the wooden rollers, $W_1$, and the tarring roller, X, where it experiences a moderate pressure. Over the roller, X, is an iron box, K, which can be heated. It has the form of a triangular prism, and is filled with hot tar. Its width must be somewhat greater than that of the fabric. At the lower edge of this box is a narrow slit, into which a very accurately fitting prism of metal, P, goes. P can be raised or lowered by a screw working in a nut. The more it is raised the wider is

the stream of tar reaching the fabric, and the workman has to regulate its position so as to get the proper rate of flow. The roller, X, has a sharp scraping or bearing upon it which removes the excess of tar, and being grooved carries it off to a receptacle where it is stored for further use. If the outflow opening is properly regulated and the fabric travels at the right rate, a fabric can be uniformly covered with tar by this simple machine. To make the coats still more uniform, the fabric is passed under the arrangement of brushes, B, which spreads the tar out quite uniformly.

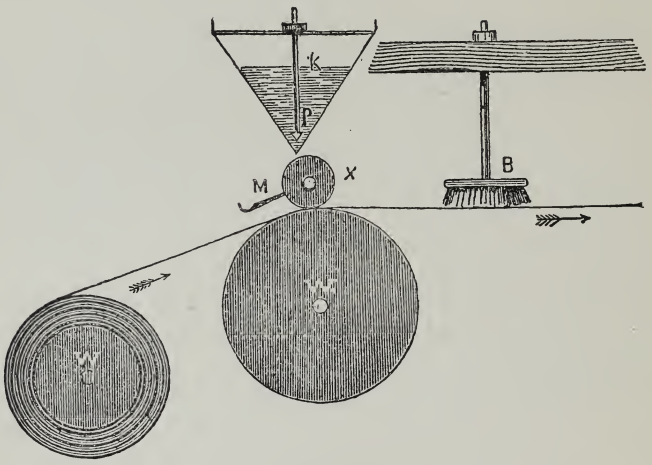



Fig. 25.

To work the whole apparatus two men are required, one to control the flow of tar and see to the spreading, the other to turn the roller, $W_1$, and see to the feed of the fabric to the tarring apparatus. When the roller, W, is empty it is replaced by a fresh one, so that the process goes on without interruption. Another spreading machine is shown in Fig. 26. The fabric to be tarred is wound on the roller, W, so as to be easily unrolled. Before meeting the tar after leaving W, the fabric is strongly pressed between the rollers, CC.

From 40 to 60 inches from CC is another pair of rollers, $C_1C_1$. While the rollers CC may be of wood, $C_1C_1$ must be of hollow metal, which can be heated by steam or by filling them with a red-hot stuff. The tar holder, T, is placed above the fabric and between CC and $C_1C_1$. To enable T to hold a lot of tar it is provided with a jacket, KK, whereby it can be kept hot by steam, or, if steam is not available, by hot water, or, still better, hot solution of chloride of calcium. The tar flows out through a flattened tube as wide as the fabric and just

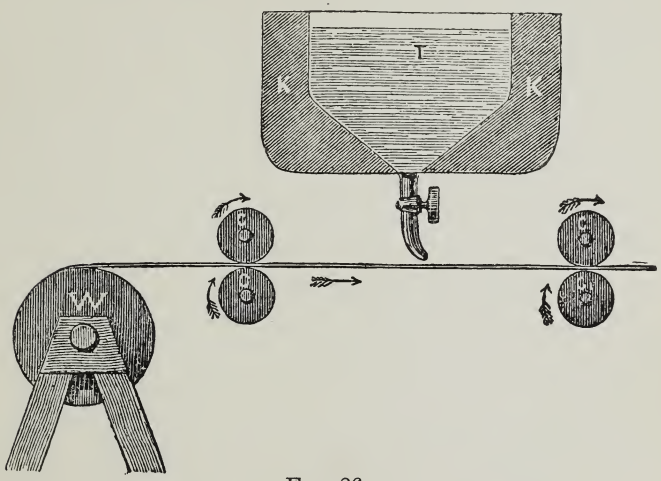



Fig. 26.

above it. The opening of the tube is regulated by a valve, so that the tar can be made to flow in streams of different thickness.

The quantity of tar required depends entirely on its nature. If the fabrics are thick and close, and not easily penetrated by tar, and if the tar is very fluid it must flow out in a very thin stream. This will ensure a perfectly uniform coating of the fabric. If, however, the fabrics are loose and porous, they absorb a good deal of tar, and, in this case, the

tar should not be very hot, so that it comes less fluid on to the cloth. The fabric travels during the tarring at a speed which will admit of note being taken as to whether the tar is being spread uniformly. If this is not the case, if, for example, the selvedges remain tarless, the workman must tar them quickly with a brush before they reach the second pair of rollers.

The uneven spreading of the tar on the fabric is a sign that the opening of the outlet tube is too narrow and that it must be widened. The fault may also be caused by the tar being too cold. It must also be noted that a width of 2 to 3 centimetres of the edge of the cloth should escape the outlet tube if the tar is flowing freely, for in that case the strong pressure of the metal rollers will spread out the tar so as to cover the vacant edges. The pressure of these rollers should be such that the whole mass of the tar is pressed between the fibres, and appears almost lustreless as it emerges from between them, and is quite lustreless when cold, and will not rub off on the finger.

A cloth properly prepared in this way should transmit no light if held up between the eye and the sun, as the pressure of the metal rollers should have filled up all the pores. Another test is to make a pouch of it, tar inside, and fill the pouch with water. The outside must not get wet. A fabric which has just been properly tarred should be black only on the tarred side. The other side should show the unchanged colour of the fabric, as the tar should only penetrate about two-thirds of the thickness of the cloth. The cloth will then be perfectly supple, and there will be no fear of its cracking when folded sharply. After being spread, the tarpaulin must be hung up for a long time in an airy shed, into which, however, rain cannot get, or in drying rooms such as those already described. This hanging is necessary for two reasons:—

1. It is very difficult to boil the tar so thoroughly that it loses all its smell. The finished cloth generally retains a

strong smell for some time, which gradually disappears when the cloth is hung up, in proportion as the volatile matters evaporate.

2. Freshly tarred cloths, if rolled up, heat so greatly that they are very liable to spontaneous combustion.

On this account drying rooms which are warmed, and through which hot air can be forced, are to be preferred to all others, as they dry the tarpaulins and make them free from smell very quickly.

If heavy tarpaulins, *i.e.*, those coated on both sides, are being made, the pressure exerted by the finishing rollers is small, so that the tar is only gently driven into the fabric. These cloths have the disadvantage of great weight and stiffness, and when folded they are very liable to crack at the folds. A properly made and dried tarpaulin must not dirty a finger forcibly rubbed over it, and even if it is stiff must not be brittle. Tarpaulins should be kept rolled up and not folded, as they then last very much longer. They always involve fire risk on account of the inflammability of the tar.

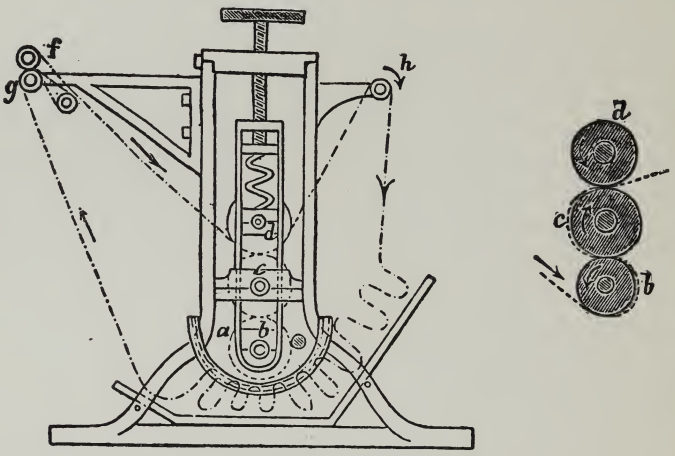
Tarpaulins are made from strong fabric woven of hemp, linen, and especially jute, a fibre which is very strong in proportion to its weight.

Honzeau and Maison mix the tar with lime soap, got from the waste soap baths of dye-houses by precipitating them with slaked lime. The tar is mixed with the lime soap in proportions depending on the degree of fineness of the cloth used. The mixture keeps well for a long time. Indiarubber is also used in it to give the tarpaulin more elasticity. Prepared by this method they are said to be waterproof, and neither to flake off nor to become sticky.

Dubret recommended the use of wood tar, either alone or combined with hydrate of alumina, instead of gas tar. He mixes 100 lb. of wood tar with a solution of 10 lb. of alum in 20 gals. of hot water and 5 lb. of caustic ammonia. After well stirring and settling, the water is poured off from the tar,

and the latter is heated with uninterrupted stirring till all the water in it has been evaporated. The final product is then spread as above on the fabric.

Döring uses wood tar oil (oleum rusci) mixed with its own weight of black wax. According to him a special machine is indispensable for working with method. It is shown in Fig. 27, where *a* is a steam-jacketed box in which the waterproofing mass is kept hot. The rollers, *b*, *c*, *d*, are of chilled cast iron; *c* and *d* are hollow and are heated by steam. The




Figs. 27 and 28.

screws, *e*, press by means of very strong spiral springs the rollers *b* and *d* against the roller *c*, which is fixed and drives the rest of the machine. *f* is a width-stretcher and *g* and *h* are hollow rollers; *h* is turned in the direction of the arrow by a chain (not shown) from *c*.

The lower roller, *b*, carries the waterproofing mass on to *c*, which, being heated, becomes covered with a very thin uniform sheet of the fused stuff, which it transfers to the fabric passing between it and *d* at such a pressure (about 25 cwt. on each spring) that the pores of the fabric are thoroughly

penetrated. After two passages the fabric is prepared on one side. It can then be turned over and the other side coated.

It is of the utmost importance that the tar oil and wax mixture should have the proper consistency, and this chiefly depends on the tar oil, only the best kinds of which should be used. They should not be used thicker than a thin-flowing tar, even if they leave the impregnated fabric still sticky. If only a very heavy thick tar oil is at command it should be diluted with oil of turpentine or camphor. The impregnated fabric is freed from light tar oils and from ethereal oils, if

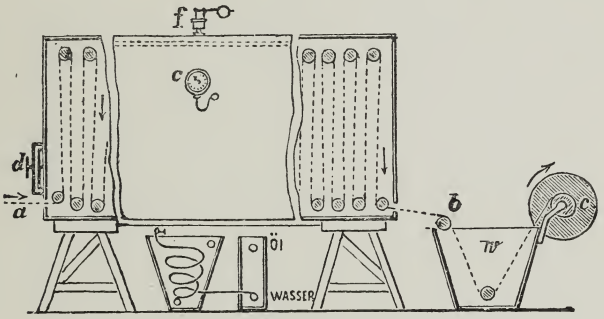



Fig. 29.

such have been used, by heating by steam or, better, by hot air. Steam is used for the purpose for half an hour at a pressure of 22 lb. The steaming is done in an iron chest, such as is shown in Fig. 29. It may be made large enough to treat several tarpaulins at a time.

It should be noted that it is desirable to run the tarpaulin through the machine by unrolling it from one roller and rolling it up again on another. As it emerges it passes through water in *w* to cool it and prevent it from being too sticky to be rolled up. As soon as the apparatus is to be put in action, a workman goes into it through the manhole, *d*, and puts a piece of uncoated cloth over the rollers inside.

The coated cloth is sewn on to one end of this and so is drawn through the apparatus. Water is not put into *w* till the uncoated cloth is all wound up on *c*. The use of hot air in the chamber is to be preferred to that of steam. The apparatus is provided with a pressure gauge and a safety valve, *f*.

The steam issuing from the chamber is charged with the vapours of light tar oils and is taken through a condensing apparatus. The oils separate from the condensed water and can be skimmed off for other uses. After half an hour's steaming, a fresh piece is sewn on to the dried piece. The roller, *i*, is then worked, whereby the steamed piece is rolled upon it and the fresh piece is drawn into the chamber to be steamed. The goods on the roller, *c*, have to be freed from adhering water, and should be passed sharply through the brushing machine to improve their appearance and lustre. The recovered light tar oils can be used for thinning the waterproofing mass. That this process can be made use of in waterproofing with coal tar is self-evident. The steam chamber may be replaced by a several storey stretching or drying machine, enclosed so that the steam and oil vapour can be condensed.

## CHAPTER XII.

### BRITISH WATERPROOFING PATENTS.

A CAREFULLY compiled list of waterproofing patents will be a useful and fitting conclusion to this work. Probably the first " waterproofs " were the suits of armour of the men of war of long ago, leaky at the joints and altogether neglecting the first principles of ventilation. The " macintosh " of the early Victorian era was sadly lacking from this important point of ventilation, and although its great utility enabled it to overcome ridicule it was a clumsy form of waterproof. Barham, who commenced the *Ingoldsby Legends* in 1837, gives its popular nickname in the line describing the apparel of the young gentleman that Mr. Simpkinson met at Margate: " a ' carpet-swab ' and ' muckintogs ' and a hat turned up with green ". The perverted cognomen of the maker conveys very neatly the uses and appearance of the garment. Smedley, a very popular novelist in the early forties, describes a tutor as very irate with one of his pupils, who he believes has left his establishment disguised as a plough-boy. The supposed smock-frock turns out to be a macintosh, at that time just edging towards popularity.

But Mr. Macintosh certainly did not invent vulcanised indiarubber. Indiarubber cloth was made by Samuel Peal and patented in 1791, and vulcanised rubber, formed by combining indiarubber with sulphur, was patented in the United States by C. Goodyear in 1839. Mr. T. Hancock, of the firm of Macintosh & Co., patented his invention in 1843, and the firm, who were probably immortalised by the

catch-word "muckintogs," were successful in bringing the cloth into fashion. However admirable their form of waterproof garment may be, a great stride was made when the idea of making garments impermeable to rain by the use of certain minerals was hit upon. We commence the list of these waterproofing inventions with that of Mr. D. Felton, in 1877. His patent is interesting inasmuch as it describes the method of producing "chromate of gelatine," [1] which is rediscovered from time to time and boomed as a waterproofing material, not, however, applicable to garments. The patent list which follows is given in chronological order, and the abridgments have been rendered as concise as possible.

**Felton, D.** 42, 1877. Tissue is saturated with a solution of a salt of zinc or cadmium, alone, or in conjunction with ammonia, by drawing it through the solution in a lead-lined tank by means of rollers. The material is passed between a pair of squeezing rollers to remove the superfluous solution and to harden it, and is then hung to dry in a warm room. Or the bath may consist of a hot solution of glue or gelatine mixed with chromate or bichromate of potash, soda or alumina, taking care that the bath is kept in the dark. As the sheet issues from the bath it is passed at once over heated cylinders.

**Muratori, C.** 278, 1877. Silk and wool are treated with a solution of gelatine, alum and potassium silicate, or of gelatine, alum or chloride of zinc, or of alum and size. The fabric is dried on a hot cylinder, and is then treated with old olive oil. The fabric is then passed through a calendering machine. The insoluble soap or oily matter may be applied by impregnating a cloth with it and passing the cloth through the calendering machine together with the fabric under treatment. In treating fabrics of vegetable fibres, *e.g.*, hemp,

[1] When a small percentage of bichromate of potash is added to a solution of glue or gelatine and any material is passed through it, an insoluble waterproof coating forms on it on exposure to the light.

cotton, canvas, linen, etc., the fabrics are first dipped in an alkaline solution of soda or potash, then dipped into water acidulated with sulphuric acid and washed and dried. The fabrics are then treated like those made of animal fibres. These processes may also be applied to the various fibres before these are made into fabrics.

**Meiter, C. W.; Houghton, H.; and Neville, J.** 547, 1877. For leggings the material is first proofed with india-rubber and then heated with a solution of carbon bisulphide and sulphur chloride, after which the two surfaces are secured together by means of indiarubber or other gum. To prevent capillary attraction along the seams, the material, before or after being waterproofed, is treated with a solution of sugar of lead and alum.

**Healey, A. E.** 3685, 1877. The material is passed through a solution of copperised ammonia, compressed to remove excess of solution, and dried.

**Knowles, J., and Cooke, H. J.** 4, 1878. A light, elastic and reversible waterproof material is formed by coating a cloth, known in the stuff trade as "Canton cloth," with a thin film of indiarubber or caoutchouc.

**Abbott, W.** 166, 1878. Vulcanisation of fabrics having either an external or an intermediate layer of indiarubber. It is particularly valuable for made-up garments, as the seams attached by means of rubber solutions are vulcanised at the same operation. The fabrics and garments are put into a closed vessel or chamber, into which the vapour of chloride of sulphur is admitted, until the vulcanisation has been effected. If the fabrics retain any of the acid from the vapours, this may be neutralised by immersing them in a weak alkali or by subjecting them to the vapours of ammonia.

**Healey, A. E.** 174, 1878. Treating fabrics with copperised ammonia, passing the material round rollers in such a way that when it expands and becomes limp under the influence of the solution, it will not pucker and crease.

**Currie, W.** 612, 1878. A thin cotton fabric is coated on one side with a solution of rubber; the coating is afterwards vulcanised by steam, and a tweed is then united to the coated cotton fabric, so that there is on one side a woollen and on the other a cotton fabric.

**Clark, H. A.** 1335, 1878. Treating linseed oil with the vapour of sulphur, whereby a chemical combination is brought about with the production of a substance resembling india-rubber. This is then mixed with benzine and allowed to stand for some time. The benzine dissolves out any remaining fatty matter, and forms a layer at the surface, which is poured off. The mass is mixed with benzol, turpentine or camphene, and is then ready for applying to cloth to make it waterproof. Lampblack, chalk or any coloured pigment may be added to the mass before use to give greater body and consistency.

**Johnson, D.** 1832, 1878. Waterproof fabrics for garments are composed of three separate thicknesses of material, an outer fabric, a middle one of unbleached calico and an inner lining. The calico receives as many coats of dressing as will render it and the seams waterproof, and the lining is not put in until the dressing is quite dry. The dressing consists of linseed oil boiled with a small portion of indiarubber (half an ounce to the gallon).

**Gooch, R.** 2044, 1878. Crape is rendered waterproof by passing it through a solution of indiarubber combined with glutinous matter.

**Northrop, J., and Illingworth, T.** 2267, 1878. The object is to produce a strong and elastic waterproof material with a lustrous appearance. A fabric is woven of silk and cotton in such a way that most of the silk is thrown on to the top of the surface. The under surface is covered with a thin film of indiarubber.

**Burghardt, C. A.; Rowley, T.; and Salomonson, A. C.** 2340, 1878. Indiarubber waste is boiled in linseed oil to a

paste, which is again boiled in an agitating vessel together with a concentrated solution of caustic soda, carbonate of soda, caustic potash, ammonia liquor, caustic lime, carbonate of potash, ammonia, lime or magnesia, or any mixture of these. The rubber is then boiled in water, and when dried is reduced to a paste by the addition of mineral naphtha, and is vulcanised.

**Rowley, T., and Salomonson, A. C.** 2957, 1878. The object is to give a single texture fabric the appearance of a double texture fabric. A waterproof fabric is prepared in the usual way, and before the film of indiarubber or other waterproof cement has dried, it is strewn with woollen or other flocks. The material is then rolled or pressed, the superfluous flocks are removed, and after the surface has dried a pattern is printed on it in imitation of a woven fabric.

**Dickson, E. V.** 2974, 1878. The material to be waterproofed is treated in the cold with a preparation of indiarubber with bisulphide of carbon and chloride of sulphur.

**Forster, T.** 731, 1879. A method of treating indiarubber fabrics so that water shall not rise in them by capillary attraction. The single or double texture indiarubber waterproof fabric is produced in the ordinary way, and is subjected to a vulcanising process. The fabric is then evenly wetted with a solution of solid paraffin, spermaceti, wax, stearin, ozokerit or linseed in their solvents, such as coal oil, benzol, petroleum, toluol, bisulphide of carbon or turpentine. The wetting is done by passing the material over a felt-covered roller, which is kept supplied with the solution by another roller below, and the fabric is kept pressed against the covered roller by an iron roller above.

**Muratori, C., and Landry, A.** 1143, 1879. Animal or vegetable size is soaked in water and then melted, tannin and silicate of soda being added, and the whole is then boiled with a solution of potash alum till the mixture is complete, when the mass is cooled. To prepare the substance for use

it is boiled with water for some hours, more water being added to keep the liquid of the correct density, which is ascertained by a hydrometer. The bath is cooled down somewhat, and the fabric to be treated is immersed in it for a time and then spread out flat on a grating to drain for several hours, being afterwards dried in the open air or in a stove heated to not more than 50° C. It is kept in a horizontal position to ensure a uniform distribution of the composition. The drainings are returned to the bath. The fabrics are finally calendered by warm cylinders or otherwise treated. If the above treatment be applied subsequently to dyeing the fabrics, the colours are permanently fixed.

**Almond, W. J.** 2319, 1879. A thin tissue of guttapercha is compressed between two layers of fabric by hot rollers. The material may be used for ladies' dress preservers.

**Spence, J. B.** 2706, 1879. Natural metallic sulphides, preferably those of copper and iron, are reduced to an impalpable powder and mixed with molten sulphur. On cooling, the compound has great hardness and tenacity and a metallic lustre. It may be used for waterproofing paper and textile fabrics.

**Walker, J.** 4657, 1879. This composition consists of 12 parts resin, 3 beeswax, 2 glycerine and 1 soft soap, with 1 to 2 guttapercha when extra stiffness is required. The ingredients, mixed by heat, are thinned with naphtha, and the fabrics, coated with it and dried by steam, are rendered semi-transparent and waterproof without being sticky or liable to crack.

**Almond, W. J.** 5073, 1879. A thin tissue of guttapercha is placed between two cloths—wool, silk or cotton—and the three thicknesses are welded into one by compressing them with hot rollers. The resulting material is odourless and is specially adapted for ladies' dress preservers.

**Aulestia, J. M.** 4570, 1880. Soap made from good

quality carbonate of soda and best olive oil, free from grease and other impurities, is allowed to stand in filtered water for about a day. The liquid is then slowly heated to boiling and the water lost by evaporation replaced. Pure beeswax, which should be refined and whitened for delicate fabrics, is melted in an earthenware vessel and mixed with the soap solution and a quantity of boiling water. The cloth is thoroughly washed and dried and wound round a cylinder placed at one end of a table, over which it is fed to a receiving cylinder at the other end. As the cloth passes over the table it is washed over on its upper side with the waterproofing liquid, while the under side is washed over as the cloth is wound on the receiving cylinder. The cloth is then treated with a solution of alum in filtered water. Both solutions are used hot, but as the colours of many prints are not fast the proportion of alum and the temperature must be varied.

**Henley, W. T.** 1881, 1881. Waterproof fabric made by saturating the fabric with an indiarubber compound capable of being vulcanised; drying and impregnating with ozokerit of a similar hydrocarbon.

**Glafey, G.** 2581, 1881. A stain or polish impenetrable to moisture consists of one part of soap dissolved in thirty parts of boiling water and an equal quantity of carnauba wax added. The whole is boiled till the wax is dissolved and a milky solution produced. Caustic ammonia is added till the solution is clearer, and the mixture is allowed to cool. The solution is precipitated, according to the use for which it is intended, with a solution of alum, sulphate of magnesia, iron or zinc, etc., to obtain precipitates of sebacic and carnauba wax acids with the bases of the salts. The precipitates are washed out, and the compounds obtained mixed with caustic ammonia and the precipitates of the desired colour. To obtain a black colour a decoction of campeachy wood and acid chromate of potash is employed.

**Burr, H. W.** 1634, 1882. In "gossamer" waterproofs

the indiarubber coating is cured by exposure to the electric light. The curing is done during the coating process, which is effected as usual. One or more electric lights are placed so as to cast their rays on the indiarubber coating, the light being concentrated by reflectors.

**Hardinn, N.** 2029, 1882. Waterproofing fabrics by immersing them in a solution of acetate of alumina. The articles treated become waterproof, and are otherwise improved, without destroying their ventilating properties.

**Zingler, N.** 242, 1883. Kauri, manilla, or any copal gum, and a little camphor are dissolved in turpentine or methylated spirit, and the hot solution mixed with either casein, vegetable albuminous matter or animal gelatine specially prepared. The mixture is then amalgamated with gum of balata or guttapercha and masticated with a preparation of castor oil, nitrous acid and sulphur chloride, combined with paraffin oil or wax. The castor oil preparation may be replaced by oxidised linseed or other vegetable oil. A substitute for indiarubber is prepared by adding first sulphur and then the albuminous or gelatinous matter to the dissolved gums. The material can be used for vulcanising or waterproofing by adding slaked lime, French chalk, sulphur, magnesium oxide, zinc sulphate, antimony sulphate or oxidised ore.

**Weygang, C.** 2251, 1883. Waterproof compositions are produced from paper pulp by sizing it with size that has been prepared by adding to it an alkaline silicate with hydrochloric acid, sodium hyposulphite and ammonium sulphate.

**Gademann & Co.** 4921, 1883. Waterproofing articles or materials of vegetable fibre, wool or leather, by soaking them in a solution of oleate or palmitate of alumina in petroleum, ether or benzine. The superfluous liquid is removed by pressure, and the articles are then allowed to dry.

**Sweet, J. S.** 133, 1884. The fabrics are soaked in a composition of linseed oil, olive oil, palm oil, oil of carraway,

soft soap and driers, and then slowly pressed between rollers. After drying, the fabrics are passed between cylinders slightly heated. They are again passed through the composition a second or third time as required, and finally through a calendering machine.

**Frankenburg, I.** 3760, 1884. The yarn for the warp (or weft, or both) is coated with a solution of rubber previous to weaving, and afterwards coated with farina to facilitate weaving. Or the warp may be passed through solution of rubber in the loom. The woven fabric is hot pressed by calender rollers to soften the rubber and cause it to fill up the interstices.

**Frankenstein, P.; Frankenstein, L.; and Wicks, R. P.** 5280, 1884. A method of producing an ornamental metallic lustre in finishing waterproof fabrics. The surface is first prepared by giving two coatings of proofing mixture and then acidising with carbon bisulphide. It is then coated with a "finish," prepared by mixing suitable metallic powders with rubber made into a dough with naphtha. A final coating of rubber solution is given to protect the metallic finish.

**Dillies et Cie.** 5317, 1884. For preserving the tissues they are dissolved in water, dried in the air, and then put in a bath of tannic acid and water containing, in some cases, birch bark oil. After soaking, they are removed and dried, being then proof against decay. To render them waterproof they are put into a bath of linseed oil (500 litres), birch bark oil (20 to 25 litres), litharge (1 to 2 kilogrammes), white lead (1 to 2 kilogrammes), talc (1 to 2 kilogrammes), and in some cases sulphate of iron (1 to 4 kilogrammes). All these substances are boiled together and allowed to cool to 200° C.; 10 to 20 kilogrammes of ceresine or other wax are then added.

**Hebblewaite, J., and Holt, E.** 6399, 1884. After the application of the waterproof coat the fabric is overspread with farina, powdered soapstone or other suitable powder,

and embossed by rollers or in any other suitable manner. Either before or after embossing, the farina is fixed by exposure to the vapours of chloride of sulphur and bisulphide of carbon. The embossed fabric may be afterwards vulcanised.

**Lister, S. C., and Reixach, J.** 7830, 1884. To prevent injury to imitation sealskin fabrics by wet, the yarn employed in their manufacture is waterproofed before weaving, or the piece is waterproofed afterwards. The waterproofing is effected by applying a solution of birch oil in methylated spirit, or of a carbon fat in benzoline, and subsequently drying.

**Company for Manufacturing Waterproof Fabrics.** 10600, 1884. Fabrics of linen or hemp, after a preliminary treatment by immersion in baths of sulphuric acid and of ammonia, are steeped for three hours in a solution of a mixture in water of colophony, crystals of soda, soft soap, silicate of potash and caustic potash. Subsequently the fabric is deposited for an hour in a bath of water, containing about 5 per cent. of sulphate of alumina, rinsed and dried. Finally, a coating of a mixture of a little paraffin, Japanese wax or palmitine and colophony is applied by rotating brushes.

**Hiller, O. B. E.** 14725, 1884. Aluminium acetate is prepared by acting on eighty parts of aluminium sulphate with 470 parts of lead acetate. The resulting solution is strained off from the lead sulphate and should be perfectly free from lead. It is diluted to 1 litre and mixed with a solution of albumen containing 12 to 15 grammes to 60 of water. Fabrics to be waterproofed are saturated with the liquid described above, dried, and passed between hot rollers to coagulate the albumen.

**Best, T. F.** 15121, 1884. Cellulose, after treatment with nitric and sulphuric acids, is saturated with a solution of sulphurous acid and heated at 100° F. in a closed vessel,

until the excess of nitric acid has been decomposed. The excess of acids is then removed by pressure, and 10 to 50 gals. of water are added for every 50 lb. of the mass, which is washed to remove all traces of free acids, and afterwards submitted to a bleaching process, if necessary, washed with warm water and dried. Crude camphor is dissolved in its own weight of methyl alcohol and filtered into a closed vessel through a mixture of fused calcium chloride with charcoal. From 55 to 65 lb. of this camphorated solution are added to every 50 lb. of the treated cellulose, the result being ready for rolling or pressing. The material may be made less inflammable by adding 12½ to 25 per cent. of magnesium borate, and may be used in a semi-plastic condition for waterproofing.

**Alexanderson, N. A.** 15923, 1884. The substance to be waterproofed is soaked in a solution of a salt in a "basic" condition, rinsed in water and dried. The salts most commonly used are "basic" alum or other aluminium salt, aluminates and chromium or iron compounds. The invention is applicable to waterproofing cloth, wood, paper, etc.

**Hallett, B., and Wiley, T. F.** 5512, 1885. A method of applying waterproofing material to pile fabrics and other goods, such as feathers. The material is deposited thereon in the form of fine spray produced by any form of appliance, the fabric being held by hand in position or carried by an arrangement of rollers.

**Frankenburg, I.** 6008, 1885. An apparatus for "curing" waterproofed fabrics or for applying farina, chalk or other substance thereto, and consists mainly in enclosing such apparatus in a chamber or casing with a chimney for carrying away fumes and dust from the operatives. A fan may be employed to draw off the fumes, and acid fumes may be neutralised by ammonia.

**Sandron, A.** 6509, 1885. This is intended specially for linen. The material is first steeped in liquid rich in tannic

properties, such as tincture of chestnuts infused in water at a temperature of 80° C. After drying, it is treated in a second bath prepared as follows: To 100 kilogrammes of boiled linseed oil, rendered very siccative, is added 100 kilogrammes of a substance rich in colouring matter free from metallic oxides and siccative, from 10 to 25 kilogrammes of essence of birch bark and 10 kilogrammes of wax which melts at a high temperature. The linen is dipped in the bath, which is raised to a temperature of 100° to 120° C., and the superfluous liquid removed by passing it between the rollers; to give a better appearance, the material may be passed through a cold bath of linseed oil rendered very siccative. It is claimed that the fabrics are not rendered sticky nor brittle, and the ordinary properties of the material remain unimpaired.

**Slade, W. H.** 10554, 1885. "One-sided terry cloth" is coated with waterproof solution on one side. When required as a reversible cloth, this is doubled over with the waterproof layer inside. Sometimes the waterproof side is lined. The fabric is of use for sponge bags, dress preservers, bandages, bibs, knickerbockers, pilches, aprons, sheets, gloves and shoe socks.

**Abbott, W.** 12079, 1885. A material which has been treated by the "rainproof" or "water-repellent" process, and which has also been waterproofed in parts, is used for making waterproof garments. The garment is so cut from the material that the portion which covers the shoulders and the upper part of the wearer consists only of the water-repellent portion of the material, while the rest of the body is covered with the waterproofed portion.

**Wiley, T. F.** 15906, 1885. The fabrics are first impregnated with a waterproofing agent, such as a solution of sugar of lead, alum or soap, and afterwards coated with indiarubber or paraffin wax by means of a solvent. Two pounds of hard white soap, for instance, dissolved in 6

gals. of water, are heated to 100° F., and used as a bath through which the cloth is passed several times, and is squeezed between each saturation. It is then treated in a similar manner with a solution of 2 lb. of alum in 4 gals. of water, and dried by steam cylinders. After passing through water at 200° F., and again drying, it is treated with a solution of 4 oz. of indiarubber and 4 oz. of paraffin wax in 1 gal. of benzoline, which is sprayed on to it.

**Frankenburg, I.** 208, 1886. Two or more coats of polish are applied to waterproof fabrics at one operation by passing the roll of cloth first over a roller revolving in a trough containing varnish, then round a drying cylinder, and then round a successive series of polishing rollers and drying cylinders until the required number of coats have been applied.

**Mandleberg, G. C.** 243, 1886. Embossed double texture waterproof fabrics are formed by spreading cement on one or both of two indiarubber waterproof fabrics and then passing them through an embossing machine. Embossed single texture waterproofing fabrics are formed by spreading the proofing upon the fabric, polishing or varnishing, embossing the proofed side of the fabric, and finally vulcanising the same.

**Haug, J. J., and Hoffmann, C.** Skins of hares, rabbits and other small animals are, after cleaning and removal of hair, boiled with 5 per cent. of crude glycerine and as little water as possible in a Papin's digester until completely dissolved. For waterproofing compositions, one quarter part of ox gall is added, and soft water to give to it a consistency of treacle, and a quarter part of chromate of potassium is added.

**United States Waterproofing Fibre Co.** 2616, 1886. Textile fabrics are rendered waterproof by being coated with or immersed in a composition consisting of resin and paraffin wax mixed together by the aid of heat and then thinned with benzine. In some cases paraffin oil may be substituted for the wax and turpentine for the benzine.

**Chevallot, E.** 3095, 1886. The waterproofing substance, such as aluminium acetate, is fixed on fabrics of all kinds by immersing the latter in a bath consisting of a mixture formed by treating an emulsion of casein with slaked lime, and then mixing therewith a solution of neutral soap.

**Freely, E. M.** 6953, 1886. To destroy the disagreeable odours emanating from substances used in vulcanising and dissolving the rubber, the fabrics are treated in one, or successively in both, of the following solutions: (1) salicylic acid dissolved in alcohol; (2) the barks of oak, hemlock and sumac, extracted by water, with the addition of salicylate of soda, Russian jachtan extract dissolved in alcohol, ether and salicylic acid.

**Orlay, C.** 10828, 1886. Fabrics are first waterproofed by treatment in successive baths of aluminium acetate, soap and alum; they are then dried at 36° to 40° C., and the proofing material is fixed by coating or impregnating them with a mixture of paraffin, wax and vaseline.

**Punshon, R.** 11427, 1886. Cloth, linen and cotton goods and other similar materials are waterproofed so that they remain pervious to air. The fabric is first washed with a hot, weak solution of alkali, which is afterwards removed by washing with hot water and drying at about 100° F. The fabric is then immersed in a hot mixture of white paraffin wax and cotton oil, to which are added, when cloth is being treated, resin and oil of turpentine, and passed through a wringing machine, after which it is dried at a temperature not exceeding 120° F.

**Wilson, G. F.** 8167, 1887. The fabrics are first saturated with a soap solution, containing either sugar soap, extract of soap, soap powder or hydroline. After being saturated the fabrics are placed, without being wrung, in a precipitating solution containing alum, lime or either blue, green or white copperas of vitriol. The fabrics are then removed and are dried without being wrung.

**Warner, C. B.** 13593, 1887. The article is immersed in or treated with a solution prepared by dissolving india-rubber in pentane and benzine, diluting with heptane or pentane, clarifying by sedimentation, and adding a little solid paraffin. The solution may be bleached by hydrobromic acid gas. The excess of solution is removed in a closed chamber, and the volatile solvent distilled by passing a current of steam or carbonic acid gas through the chamber, or by a reduction of pressure. The article is finally dried at a temperature of 100° to 150° F. The article must also be treated with a vulcanising agent when required for use at temperatures which would soften rubber. The exit and entrance tubes of the evaporation chamber are closed with diaphragms or bunches of fine wire.

**Mandleberg, G. C.** 16541, 1888. Waterproof garments, especially those for ladies, free from disagreeable odour and scented with an agreeable perfume, are made by preparing the cloth or fabric in the following manner: The fabric is first coated with a dough formed of indiarubber, litharge and naphtha solvent; secondly, with several coatings of a dough of rubber, litharge, sulphur and naphtha; and, lastly, with a dough like the first described, but with a smaller proportion of litharge. Farina is then applied to the surface, which is partly vulcanised, and the garments are made from it in the ordinary manner, dried in an air stove, and then completely vulcanised and scented with oil of lavender or other volatile oil.

**Mandleberg, G. C.** 16542, 1888. Rubber-proofed fabrics, before being made up into garments, are vulcanised by the cold process, and farina is applied to the proofed surface before, during or after vulcanisation. By using deodorised naphtha in the preparation of the dough, the necessity for a high stoving temperature is avoided.

**Mandleberg, G. C.** 16543, 1888. The dough used in preparing fabric for making indiarubber waterproof garments is obtained by dry-kneading the indiarubber and soaking in

deodorised naphtha in a closed vessel, before working between rollers, and spreading upon the backing.

**Oliver, W.** 2873, 1889. Stretched American cotton duck or other cloth is coated with a composition consisting of oxidised oil and whiting or other mineral whites, with a small proportion of indiarubber dough. The fabric is next rolled, and then dried by being passed over heated cylinders, after which it is folded into the requisite number of plies and stitched. The edges are treated with a solution of shellac.

**Mandleberg, G. C.** 3726, 1889. The dough of the first coat contains indiarubber, litharge and sulphur dissolved in naphtha. The following coatings contain more sulphur and the final coating no sulphur. A surface of farina is then put on, and the fabric first vulcanised by dry heat, and finally hardened by the liquid, or cold vulcanising process, or by the vapour process. After the garments are made up in the ordinary manner they may be scented.

**Greening, F.** 5344, 1889. A base for the waterproofing composition is prepared by treating cotton combings, paper, esparto grass or rags with a mixture of fuming nitric acid and sulphuric acid. After washing, the material is treated with ammonia, alum and sodium chloride, and again washed. The solvent is prepared by distilling acetate of lead and anhydrous lime and mixing the distillate with fusel oil or hydrocarbons. Purifying agents, such as phosphoric chloride or potassium carbonate, are added, and the distillate is again distilled. Absolute alcohol is added to the final distillate. The material may be coloured with aniline dyes or ordinary pigments. When required as a liquid coating or varnish, the proportion of the solvent is increased.

**Gaugl, M., and Mössner, J.** 5763, 1889. Solutions of neutralised isinglass, lead acetate and alum are mixed. The solution, after standing, is filtered and diluted as required. The goods, such as cloth, felt or paper, are impregnated or washed with the solution.

**Dreyfus, C., and Robinson, J.** 7090, 1889. In the manufacture of indiarubber or waterproof textile fibres or fabrics, the indiarubber is dissolved in purified naphtha or any one, or a mixture of two or more, pure hydrocarbons of the aromatic series.

**Baswitz, C.** 16708, 1889. Textile fabrics are treated with an ammoniacal solution of copper obtained by dissolving copper hydrate precipitated by soda lye from sulphate of copper.

**Doller, F.** 6698, 1891. Waterproofing compositions. Textile materials are waterproofed by means of a composition obtained by dissolving guttapercha or indiarubber in molten paraffin wax, stearin or sebacic acid. The solution is applied to the cloth by rollers at a temperature of 70° C., or it may be first thinned by benzine or other solvent, the material being then drawn through it and afterwards exposed to a current. Liquid paraffin wax may be employed in place of the paraffin wax. In some cases a mixture of stearin or sebacic acid and alumina or stearin and oxide of copper or other metals, dissolved in pyridine, alcohol, benzine or other hydrocarbon, and also a solution of celluloid, celloidin or collodion in pyridine, alcohol, benzine or other hydrocarbon, may be used in addition. These latter solutions may be used alone, or in combination with each other. Liquid paraffin may also be added.

**Weir, J.** 8573, 1891. A new hydrocarbon product called "lithocarbon" occurs naturally in Texas mixed with sand or shell rock, and has the composition of a hydrocarbon, containing a small quantity of sulphur and traces of oxygen. It is extracted by acting upon the crushed rock in a vessel with a solvent, such as petroleum, naphtha, benzine, carbon bisulphide or turpentine. The substance is flexible, tough plastic at ordinary temperatures, jet black in colour and withstands a temperature of 600° F. It may be used for waterproofing textile fabrics.

**Briggs, E.** 3067, 1892. Showerproof fabrics for ladies' waterproofs, dust covers, umbrellas, parasols, etc., are woven of silk containing the natural gum. The silk is treated in the preliminary operation of preparing the thread, and in any subsequent operation of dyeing, finishing or the like, in such a manner, and at such a temperature, as not to remove the natural gum.

**Cross, C. F.; Bevan, E. J.; and Beadle, C.** 8700, 1892. Cellulose in any of its forms, such as that obtained from flax, rhea, hemp, wood or bleached cotton, is impregnated with a 15 per cent. solution of caustic soda or potash, expelling the excess by means of a centrifugal machine, and then exposing the mercerised material, which now contains 40 per cent. to 50 per cent. of alkali, to the action of carbon bisulphide in a closed vessel at the ordinary temperature for several hours. The product, on stirring with water, forms a very viscous solution of a yellow colour. The solution may be used for depositing cellulose upon textile fabrics.

**Hutchinson, T. J., and Hardman, R. B.** 11994, 1892. In order to recover the cloth from damaged waterproof fabrics, they are treated in a bath of oil or fatty matters until the proofing is decomposed, or partly or wholly dissolved. The excess of the oil or fatty matter is then expressed by rollers, and the cloth is treated with a volatile solvent for the removal of the oily or fatty matters, and the products from the proofing; or in some cases these matters may be removed by a scouring process.

**Holfert, J.** 4697, 1894. Tissues are made waterproof by covering, mixing or impregnating them with a solution of animal gelatine and then subjecting them to the action of a solution of formic aldehyde.

**Healey, A. E., and Williams, J.** 5054, 1894. A soluble chromate, such as chromate or bichromate of potash, soda or ammonia, is added to the ammoniacal solution of copper oxide employed in waterproofing paper, and fabrics such as

canvas, by the method known as the "Willesden process". It is stated that the product obtained by this method has a brighter and more durable colour, and can be more readily dyed.

**Rous, H., and West, G. N.** 5718, 1894. Textile materials are treated with chemical solutions to render them waterproof and fireproof. The first solution is made by mixing acetate of lead with alum and allowing the precipitate to settle. The second solution consists of a mixture of tungstate of soda and bromide of potassium. After being soaked in the two solutions successively, the material is steamed, dried and pressed.

**Berlowitz, M., and Salomon, S.** 6617, 1894. Fabrics are impregnated with hydrocarbons and resins in solution. After dipping in the solution, they are kept immersed in water, which prevents evaporation of the solvent. The preferred solution consists of spermaceti, paraffin wax, gum copal, colophony, indiarubber, guttapercha, oil of rosemary, bisulphide of carbon and ether.

**Turner, E. M.** 9746, 1894. Pure paraffin wax, or other wax free from grease, is dissolved in benzine, etc., and the solution applied to the fabric by dipping, brushing or spraying. After the solvent has been allowed to evaporate, the fabric is ironed to drive in the impregnating material, and is finally drawn over blunt edges to remove stiffness. In the case of silk, cloth, dress materials, etc., the solution may be applied on either side, and both sides may be ironed. In treating a pile fabric, the solution is applied to the back and the back alone ironed.

**Cohrs, H., and Oesterreich, J.** 10337, 1894. The material is heated and brushed with a mixture of water, alum, silicate of soda or potash and vaseline, after which it is dried. The process is applicable to fabrics and to finished garments, such as trousers, waistcoats, coats, mantles, hats, ladies' jackets, bonnets, etc.

**Hendricks, V.** 12954, 1894. Cloth for the manufacture of boots and shoes is treated with a solution made by mixing alum, sugar of lead and tannin, and allowing the precipitated sulphate of lead to settle. Cloth so prepared is stated to be waterproof but permeable by air. To cause the cloth to retain its properties, it may from time to time be dipped in the solution.

**Boeddinghaus, W.** 20359, 1894. Waterproof coloured flexible vegetable textile fabrics are produced by dyeing the material, before or after being woven, with coal tar colouring matters, which withstand the action of ammoniacal copper, or of the copper oxide contained therein, washing and drying the goods, and then treating them with ammoniacal copper in the usual manner, and finally drying them.

**Frankenstein, L.** 5120, 1895. Bone dust, or material of similar chemical composition, is used instead of farina for preparing rubber-coated fabrics for printing. The bone dust may be bleached, or may be dyed to form a coloured ground. The proofing is preferably vulcanised after printing, and an extra coat of proofing may be applied to fix the design.

**Verdier, R.** 3797, 1896. Imitation leghorn and other hats are waterproofed by coating them with, or immersing them in, a mixture of potassium or sodium silicate with a saturated aqueous solution of potassium bichromate.

**Electro Waterproofing and Dye Fixing Co.** 8323, 1896. Fabrics are moistened with water and pressed between two plates or rollers, between which a current of electricity is passed. The anode consists of an oxidisable metal, the oxide of which is deposited on the fibres. For white materials, aluminium and tin are the metals preferred, though zinc and other metals can be used. When a dyeing or staining of the fabric is desirable or objectionable, copper, iron or silver may be used. If the current is continued for too long, hydrogen accumulating on the cathode may reduce the oxide formed; to obviate this, a layer of cloth, etc., may be placed between

the fabric treated and the cathode. The process is stated to be applicable to cotton, linen, woollen and silk fabrics, ships' sails, string, sewing thread, etc.

**Amos & Co.** 15893, 1896. Salts of alumina or other bases, with oleic or other fatty acids, are dissolved in benzine or any other volatile solvent and applied to fabrics, paper, leather, etc. The solvent is afterwards evaporated and recovered by condensation. The fabric may be first treated with a soap dissolved in benzine and afterwards with an aqueous solution containing a salt of alumina, etc.

**Kipling, W. C., and Arnold, E.** 22197, 1896. Sulphate of alumina and acetate of lead solutions are mixed, and after precipitation solution of tannin is added. After the further precipitation which takes place, the clear liquid is ready for use as a waterproofing solution. The solution is applied to the threads after dyeing and before weaving, or in some cases to the woven fabrics.

**Coulter, W., and Macintosh & Co.** Finely divided asbestos is mixed with rubber to produce a waterproof fabric suitable for ornamentation by printing, etc.

**Stephens, E.** 5085, 1898. Waterproofing by pressing the material to be waterproofed against an endless band, previously soaked in the waterproofing solution, by pressing the two together between hot rollers.

**Newman, G. F.** 11264, 1898. A waterproofing solution having the following composition :—

| | |
|---|---|
| Boiled oil . . . . . | 6 gals. |
| Castor oil . . . . . | 2 ,, |
| Turpentine . . . . | 6 pints. |
| Patent driers . . . . | 6 oz. |
| Powdered sulphur . . . | $\frac{1}{2}$ ,, |

The mass will be coloured with yellow ochre or other pigment.

**Lawrence & Co.** 20356, 1898. A waterproofing substance is extracted from kelp by acting on it with dilute

mineral acid of a special strength. The fucose from the kelp is fixed on the fabric by an after passage through a solution of alumina or of some other metallic salt.

**Weber, C. O., and Taylor, J.** 21020, 1898. Aluminium tannate is used as a waterproofing liquid. The liquid is made for use from the following recipe: 36 lb. of sulphate of alumina are dissolved in 25 gals. of water. To this solution another is added of 61½ lb. of lead acetate in 25 gals. of water. The solution of acetate of alumina, having been removed from the precipitate of lead sulphate, is mixed with one of 1·4 lb. of tannic acid in 50 gals. of water. Calcium acetate may be substituted for lead acetate.

**Olivier, M. G.** 22104, 1898. Solution of paraffin, indiarubber and beeswax, or of two or one of them, in bisulphide of carbon, for the purpose of waterproofing.

**Good, W. H.** 850, 1899. Waterproofing fabrics are made by weaving waterproofed yarns. The threads are waterproofed by passing first through a tannin solution and then, after drying, through a dressing solution. The two solutions are composed as follows:—

| *Tanning Solution.* | | *Dressing Solution.* | |
|---|---|---|---|
| Birch bark . . | 56 lb. | Poppy oil . . | 4 gals. |
| Bichromate of potash | 4 lb. | Indiarubber solution | 4 lb. |
| Calcium chloride . | 2 lb. | Red mercury oxide | 2 lb. |
| Tar . . . | 4 pints. | Resin . . . | 56 lb. |
| Solution of alkali . | 8 lb. | Beeswax . . | 56 lb. |
| | | Palm oil . . | 28 lb. |

**Williams, J.** 1358, 1899. The objectionable colour got by waterproofing with ammonium cuprate is removed by immersion in a solution of zinc cyanide of ammonia.

**Van Gestel, J. T.** 13433, 1899. Electrolytic waterproofing and dyeing. The fabric to be waterproofed is soaked with a solution of a metallic salt. A current is then passed through the liquid, and precipitates the oxide of the metal in

and upon the fibre, thereby waterproofing it and fixing at the same time any dye that may be present.

**Staples, E. C., and others.** 20667, 1899. A waterproofing composition made from the following recipe :—

| | |
|---|---|
| Resin | 64 lb. |
| Paraffin wax | 86 lb. |
| Rubber solution | 6 to 12 lb. |
| Boiled oil | 2 lb. |

**Schlomann, H. W.** 2703, 1900. Waterproofing by depositing insoluble metallic compounds in the fibre by electrolysis, the fabric being pressed between the anode and the cathode, which are made of its shape.

**Hepburn, G. G.** 5994, 1900. Waterproofing with an insoluble tungstate, in combination with a large selection of organic substances, including oils, waxes, resin soaps, fatty acids, etc. For example, copper tungstate is heated with oleic acid, and the fabric is soaked in a solution of the product in a mixture of benzine and carbon bisulphide and then dried.

**Greening, F.** 8575, 1900. A waterproofing composition, consisting of anthracene and a copal resin, such as anime or elemi.

**Watzlawik, F.** 14555, 1900. Waterproofing by cementing several thicknesses of the fabric together.

**De la Grange, E. S.** 16332, 1900. Waterproof fabrics are made by weaving threads previously made waterproof by a mixture of 100 lb. of nitrocellulose, 15 lb. of rubber solution and 5 lb. of tin protochloride.

**Kronstein, A.** 2679, 1901. Waterproofing by impregnating the fabric with any organic substance which can then be made insoluble by moderate heat. The special substance mentioned is wood oil. The temperature required is about 200° C., and must be maintained from eight to ten hours.

**Oesterheld, A.** 10007, 1901. To prevent fabrics waterproofed in the usual way with rubber from becoming hard

and rough, the rubber composition is mixed before use with quarter to half of its weight of a heavy hydrocarbon, *e.g.*, paraffin, and is, after waterproofing, passed through a warm bath of the same substance. Hereby the goods are made supple, and all pores are closed, so that only the outer surfaces will ever need disinfection.

**Newman, G. F.** 12074, 1901. A method of waterproofing consisting in painting over first solution A and then, after drying, solution B.

*Solution A.*

| | |
|---|---|
| Boiled oil | 3 gals. |
| Castor oil | 1 gal. |
| Patent driers | 2 lb. |
| Powdered sulphur | 4 oz. |
| Mineral pigment | q.s. |

To be applied with a brush.

*Solution B.*

| | |
|---|---|
| Boiled oil | 4 gals. |
| Patent driers | 2 lb. |
| Powdered sulphur | 4 oz. |
| Mineral pigment | q.s. |

**Grenet, P.** 13562, 1901. Waterproofs that can be washed and dyed without affecting their proofness, are produced by the following method: The material is first immersed in a solution of alum, carbonate of soda and paraffin, in benzine, together, except for new garments, with soap. A second bath of solution of paraffin in benzole is then given, and the goods are dried at 90° C. It is said that the process is applicable to feathers, furs, velvets, crapes and other delicate articles, without injuring them in any way.

**Dutilleul, G.** 14106, 1901. Fabrics are waterproofed by immersion, first in a solution of 15 lb. double sulphate of alumina and 25 lb. of alcohol tannin in 100 gals. of water, drying, treating with a solution of 25 lb. of potash in 100 gals.

of water, drying again, and passing through a bath of paraffin, vaseline and heavy mineral oil dissolved in petroleum ether. The fabric is then centrifuged and dried.

**Wharton, F. M.** 15829, 1901. Waterproofing with resinates, oleates, stearates and palmitates of the heavy metals, applied hot or in solution.

**Williams, J.** 19013, 1901. A waterproofing solution made by forcing oxygen or air through a solution of carbonate of ammonia in a vessel packed with copper scraps, until solution is complete.

**Port, G. M.** 20281, 1901. Waterproofing with double palmitate of zinc and alumina dissolved in a drying oil. The palmitate is prepared by precipitating an alkaline palmitate with zinc alum.

**Menzies, J.** 12807, 1902. Waterproofing fabrics by treatment, first in a bath of soap, waterglass and paraffin wax, and then in a fixing bath of acetate of alumina, finally drying and calendering.

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